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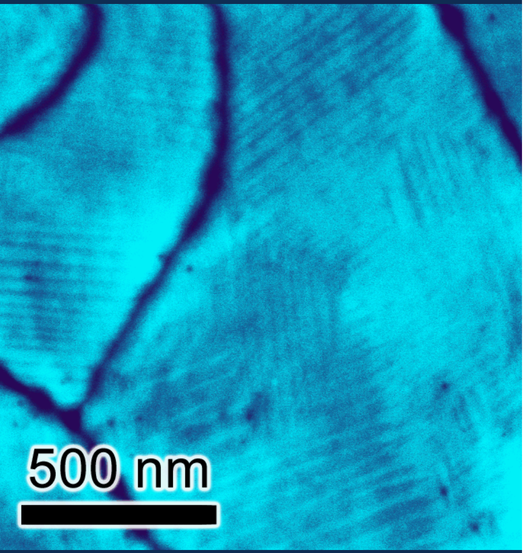

Thermal Conduction in Ferroelectric Thin Films: Size, Composition, and Domain Effects

Jon Ihlefeld

Sandia National Laboratories

Albuquerque, NM, USA

jihlefe@sandia.gov

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Collaborators

University of Virginia

- ***Brian Foley***
- ***Brian Donovan***
- ***Patrick Hopkins***

University of Connecticut

- Joseph Desmarais
- Linghan Ye
- Bryan Huey

Penn State University

- Margeaux Wallace
- Susan Trolier-McKinstry

Sandia National Laboratories

- David Scrymgeour
- Joe Michael
- Bonnie McKenzie
- Douglas Medlin
- Elizabeth Paisley
- Christopher DiAntonio
- Tom Chavez
- Mia Blea-Kirby

Colorado School of Mines

- Geoff Brennecka

Cornell University

- Carolina Adamo (Stanford)
- Darrell Schlom

Outline

- Thermal conductivity of ferroelectrics
  - Single crystals
  - Prior research on ‘extrinsic’ effects
- Our thermal conductivity/ferroelectrics research
  - Grain size scaling effects in $BaTiO_3$
  - Domain boundaries
  - Composition Effects

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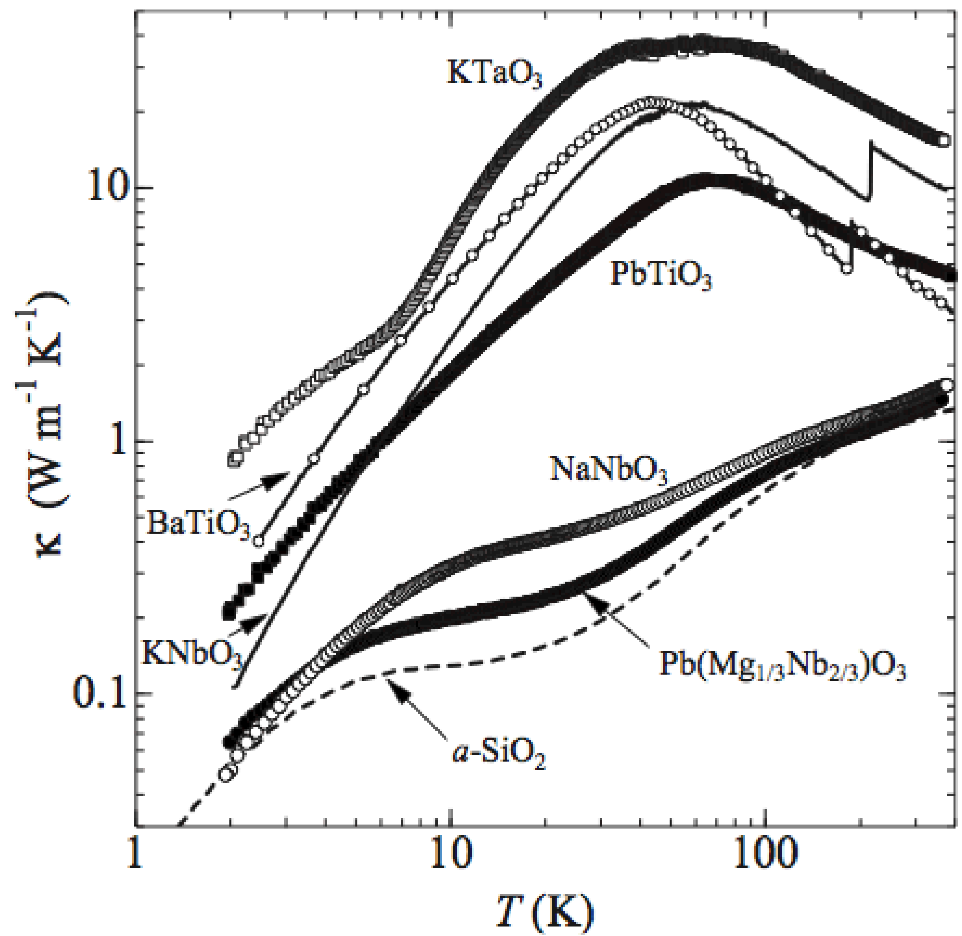
Thermal Conductivity of Ferroelectrics

- Ferroelectrics and related materials can have low and diverse thermal conductivities
  - Complex phonon spectra
  - Soft modes
  - Anisotropy
- What about extrinsic effects?
  - Grain boundaries
  - Domain walls
  - Composition
- Surprisingly limited numbers of studies on ferroelectric materials

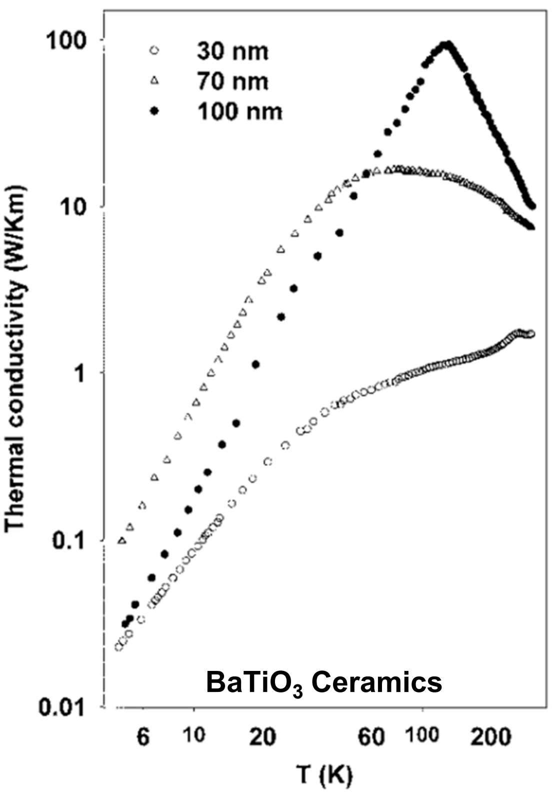
Thermal Conductivity of Ferroelectric Single Crystals



Data from: Tachibani *et al. Appl. Phys. Lett*. **93**, 092902 (2008)

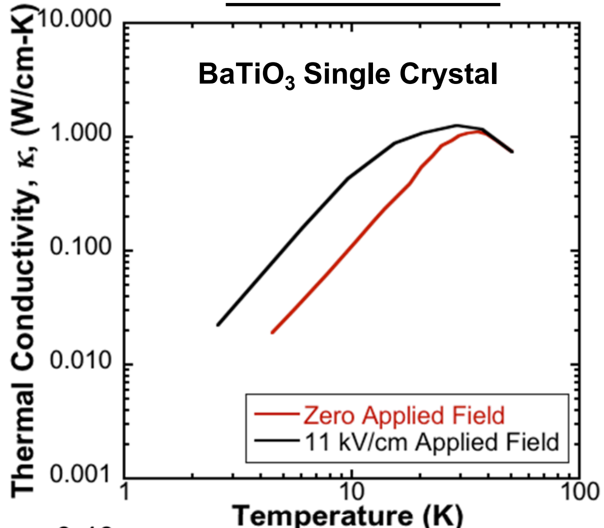
Extrinsic Effects on Thermal Conduction in Ferroelectrics

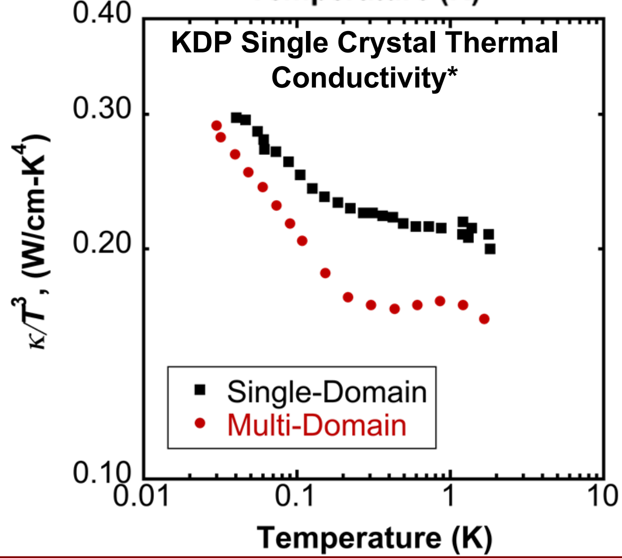
Grain Boundaries



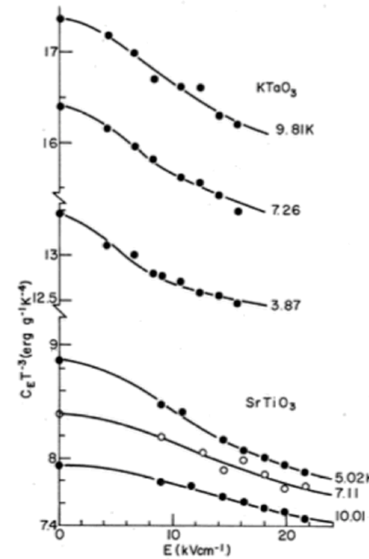
Jezowski, *et al*. Appl. Phys. Lett, 90, 114104 (2007)

Domain Walls

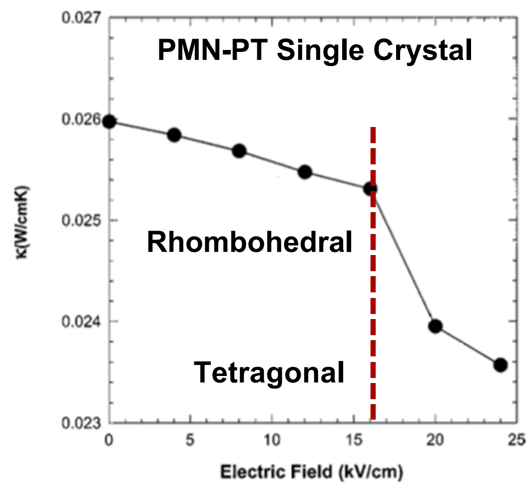




Soft Modes



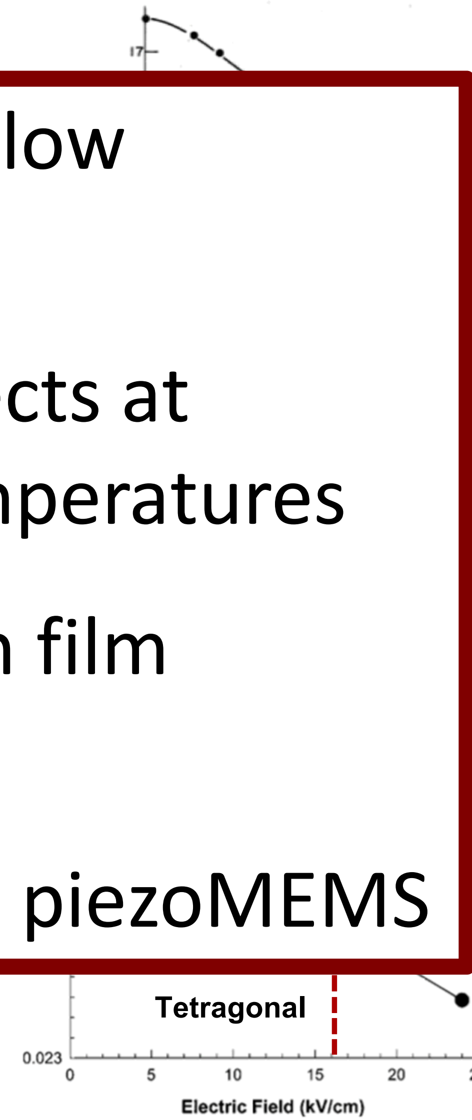
Phase Transitions



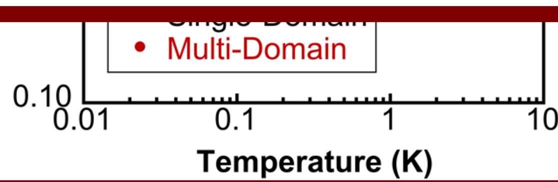
Mante and Volger, *Physica*, 1971 Weilert, *et al.*, *Z. Phys. B*, 1993 Lawless, Phys. Rev. B, 1978 Zhu and Han, *Appl. Phys. Lett.*, 1999

Extrinsic Effects on Thermal Conduction in Ferroelectrics

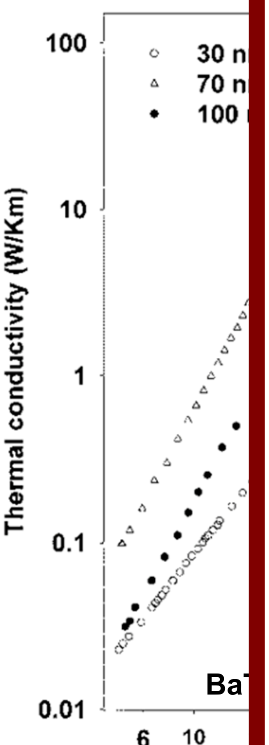
Soft Modes



Domain Walls



Grai



- Most prior work focuses on low temperature physics
- Lacking is knowledge of effects at technologically relevant temperatures
- Virtually no research on thin film embodiments
  - Important for MLCCs and piezoMEMS

Jezowski, *et al*. Appl. Phys. Lett, 90, 114104 (2017)

Mante and Volger, *Physica*, 1971 Weilert, *et al*., *Z. Phys. B*, 1993 Lawless, Phys. Rev. B, 1978 Zhu and Han, *Appl. Phys. Lett.*, 1999

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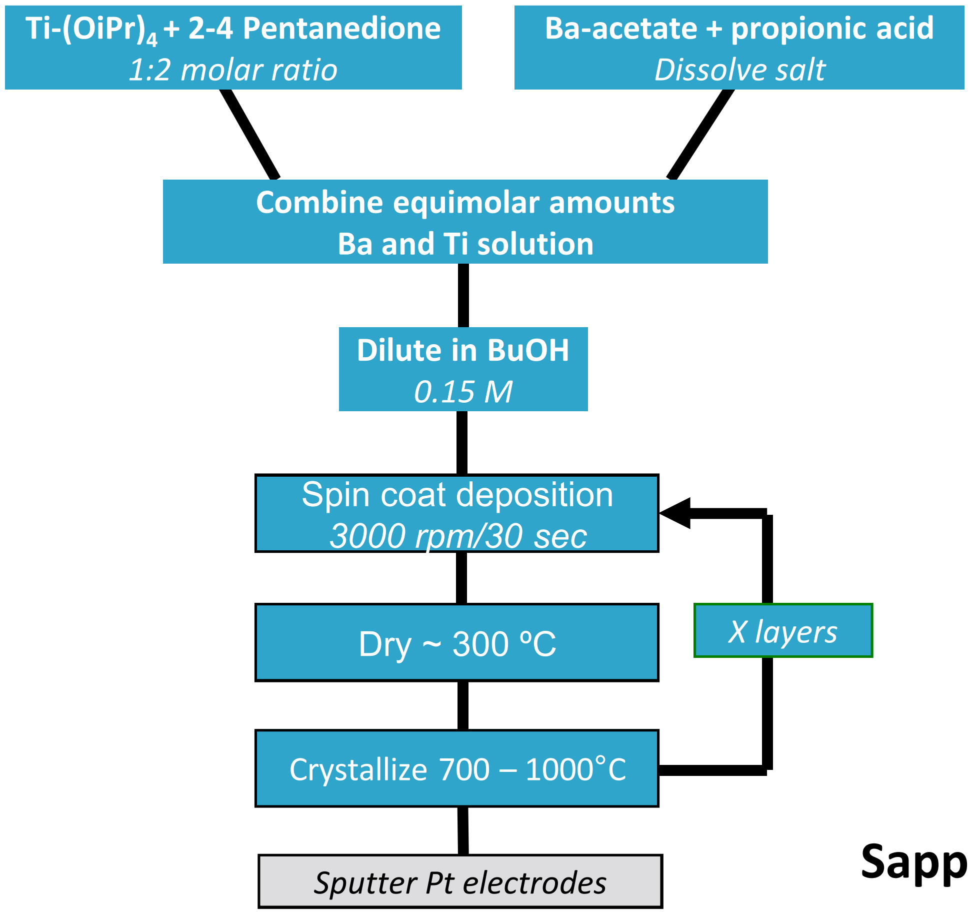
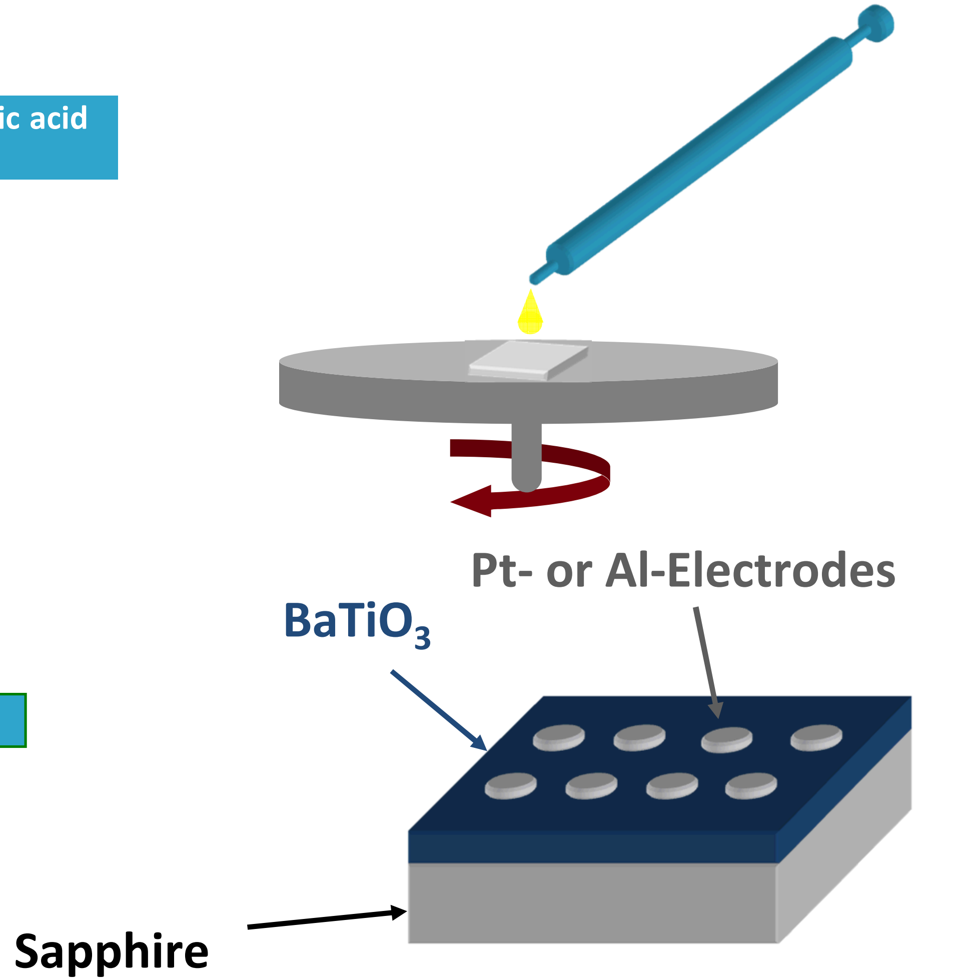
  - Domain boundaries
  - Composition Effects

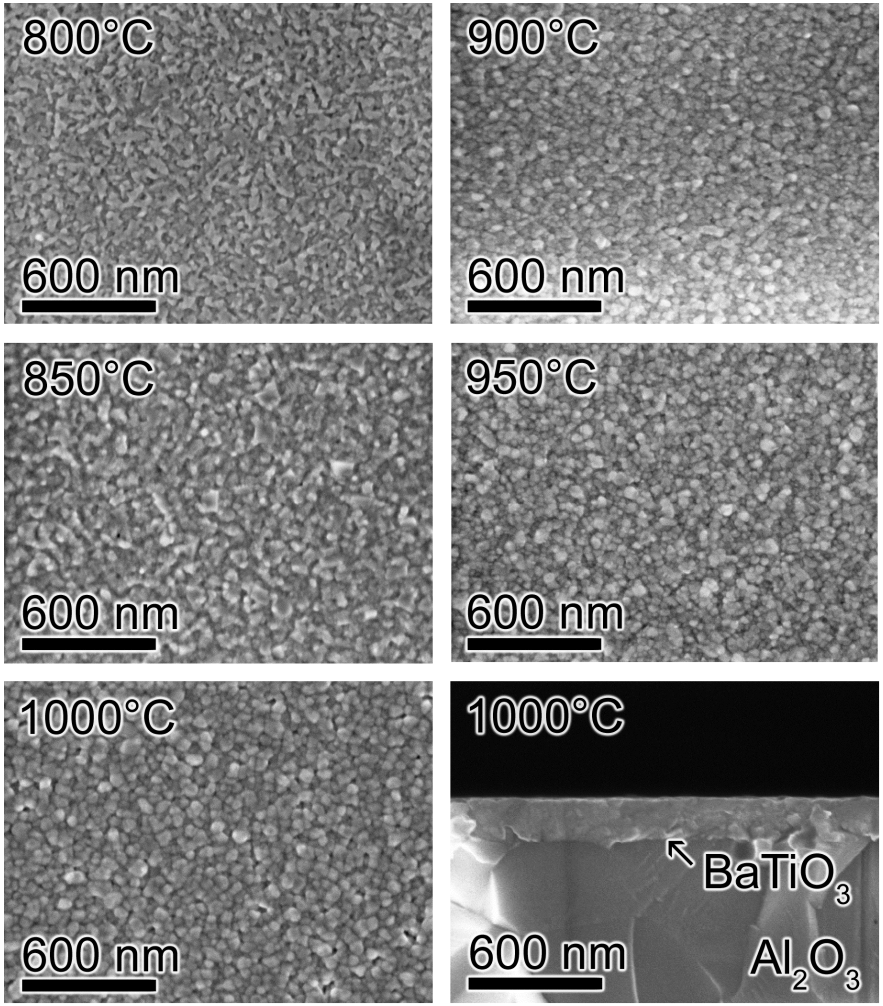
Chemical Solution Deposition and Grain Size Modification of $BaTiO_3$

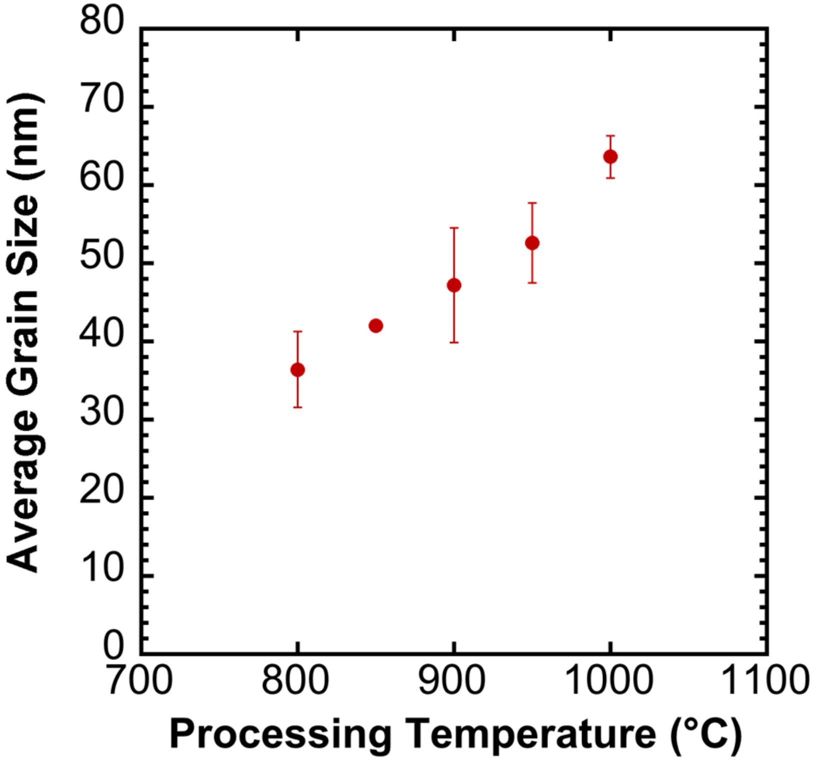




Film thicknesses: $BaTiO_3$ = 175 nm

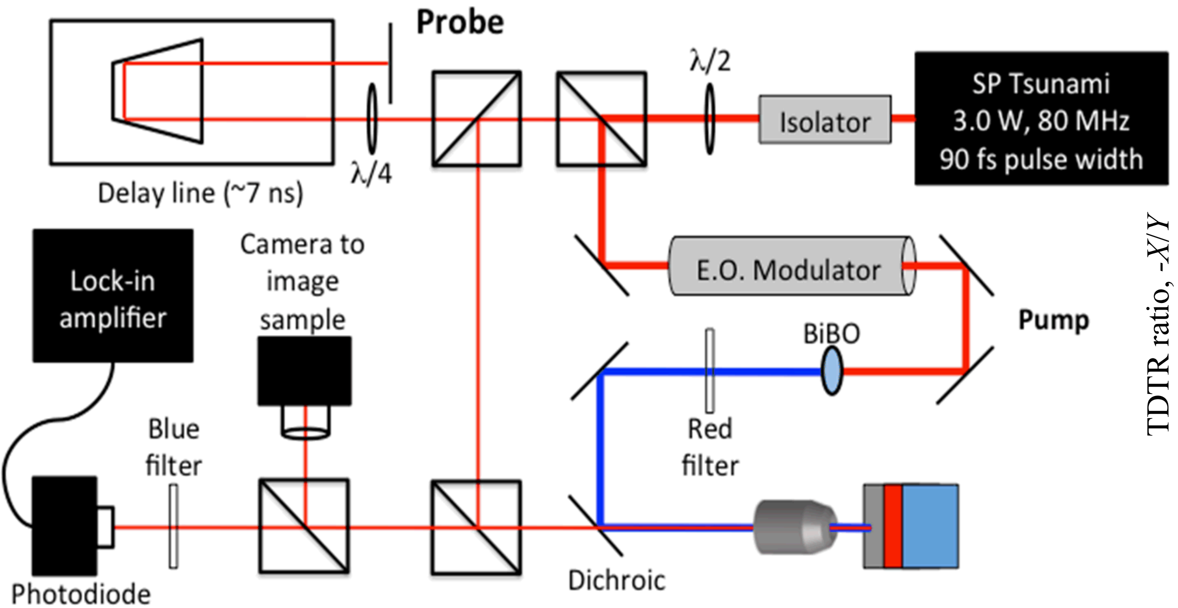
Preparing Appropriate Samples to Study Grain Size Effects: $BaTiO_3$

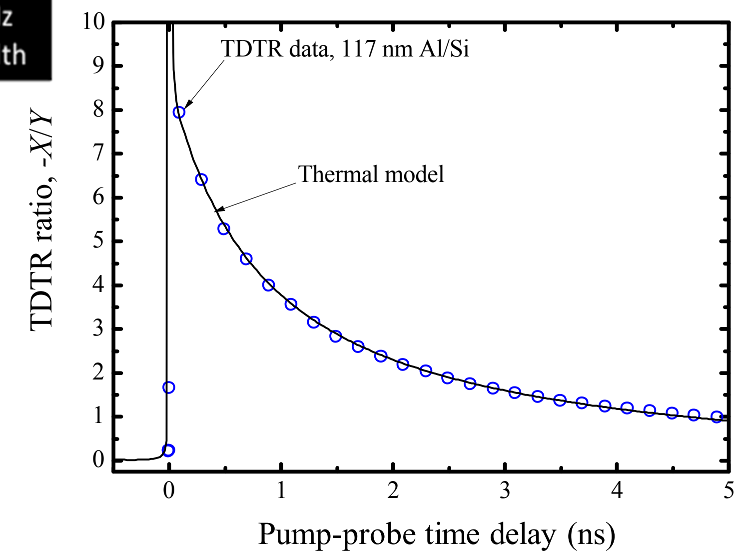


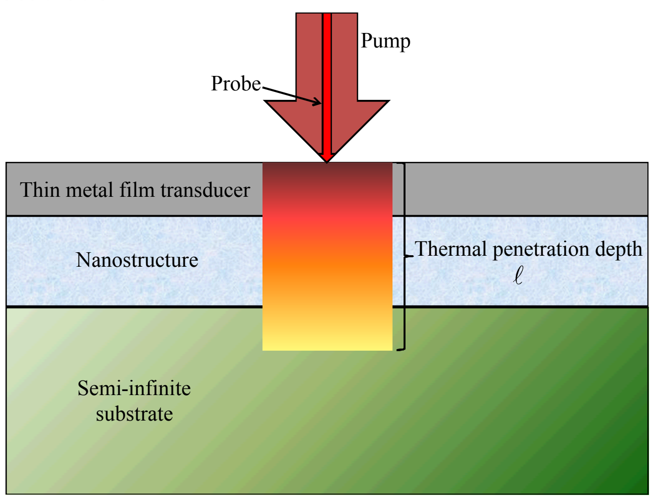


- Grain size scales with process temperature
- Films are all >97% dense
  - High-resolution SEM

Time Domain ThermoReflectance (TDTR)



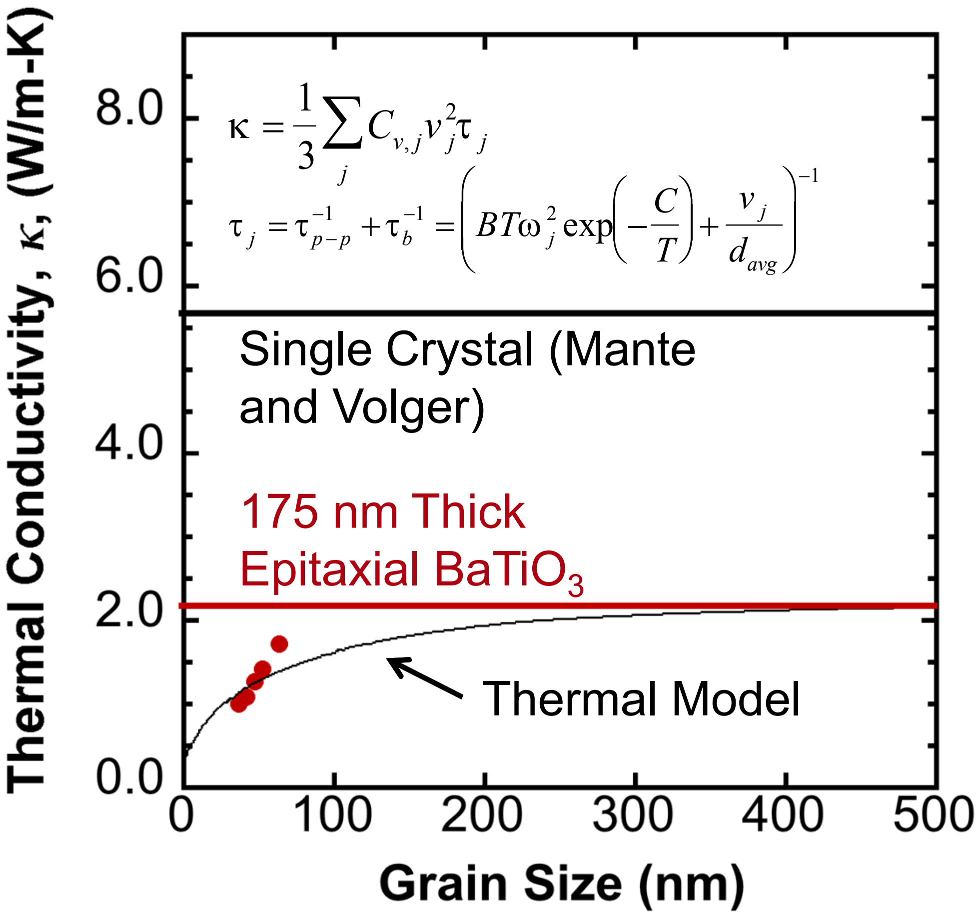




- Can measure thermal conductivity of thin films and substrates (κ) separately from thermal boundary conductance (h_K)
- Nanometer spatial resolution (~10's of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact

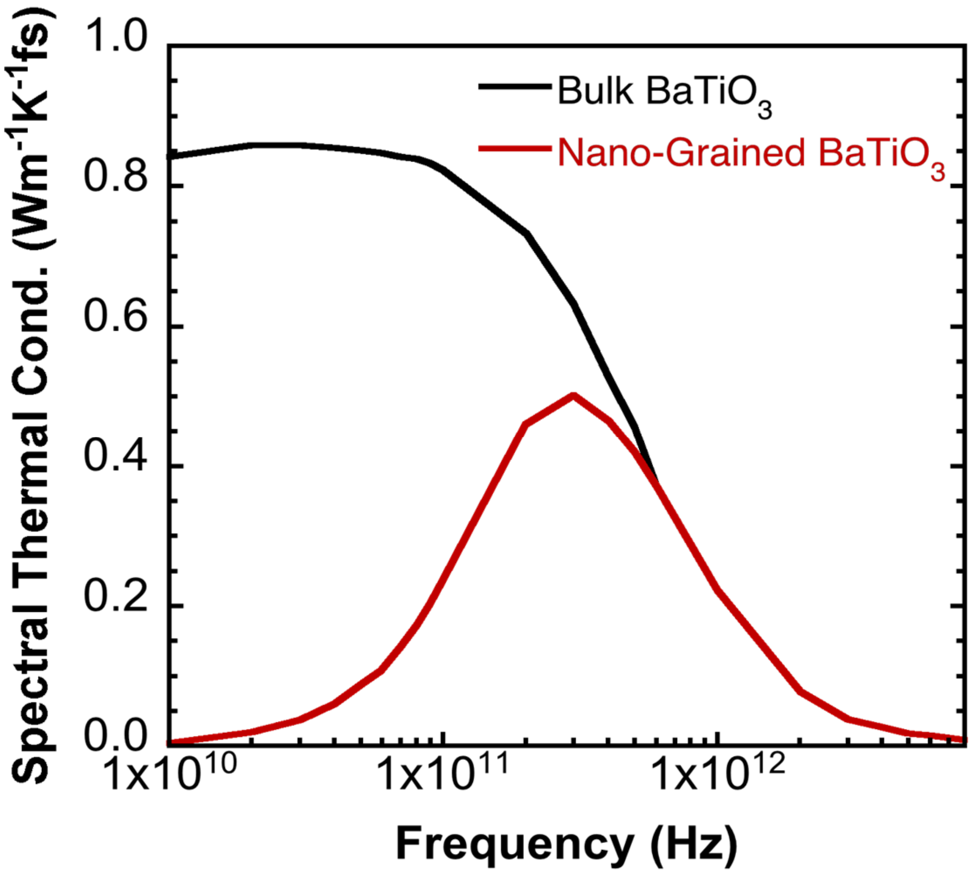
P. Hopkins *et al.*, *J. Heat Trans.* 132, 081302 (2010)

Grain Boundary Effects in $BaTiO_3$



- Room temperature thermal conductivity scales with grain size
  - Less than 3 W/m-K for all sizes
- 3X reduction in thermal conductivity from single crystal value due to nano-grain microstructure
- Thermal model fit to data accounting for scattering time from phonon-phonon interactions and boundaries
- Grain boundary scattering dominates
- ***Cannot simply consider room temperature phonons to have a single MFP – phonons have a spectrum of wavelengths***

Grain Boundary Effects in $BaTiO_3$



- Room temperature thermal conductivity scales with grain size
  - Less than 5 W/m-K for all sizes
- 3X reduction in thermal conductivity from single crystal value due to nano-grain microstructure
- Thermal model fit to data accounting for scattering time from phonon-phonon interactions and boundaries
- Grain boundary scattering dominates
- ***Cannot simply consider room temperature phonons to have a single MFP – phonons have a spectrum of wavelengths***

Outline

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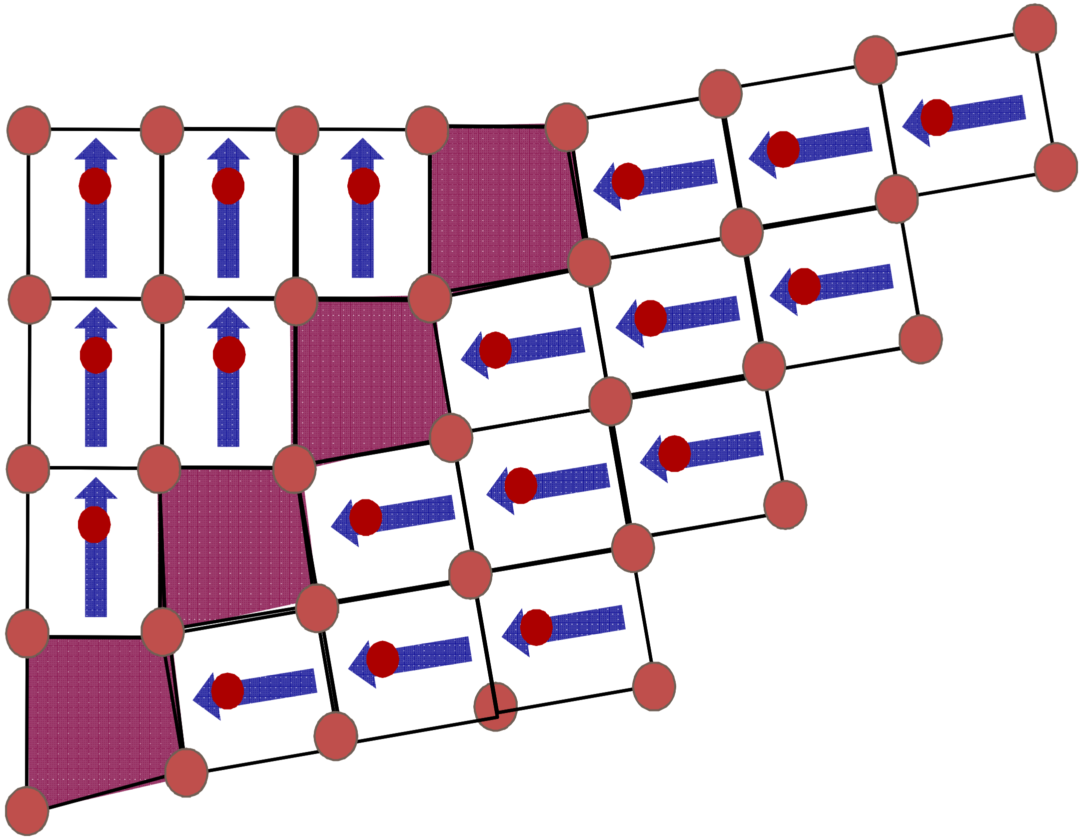
Domain Boundary Effects

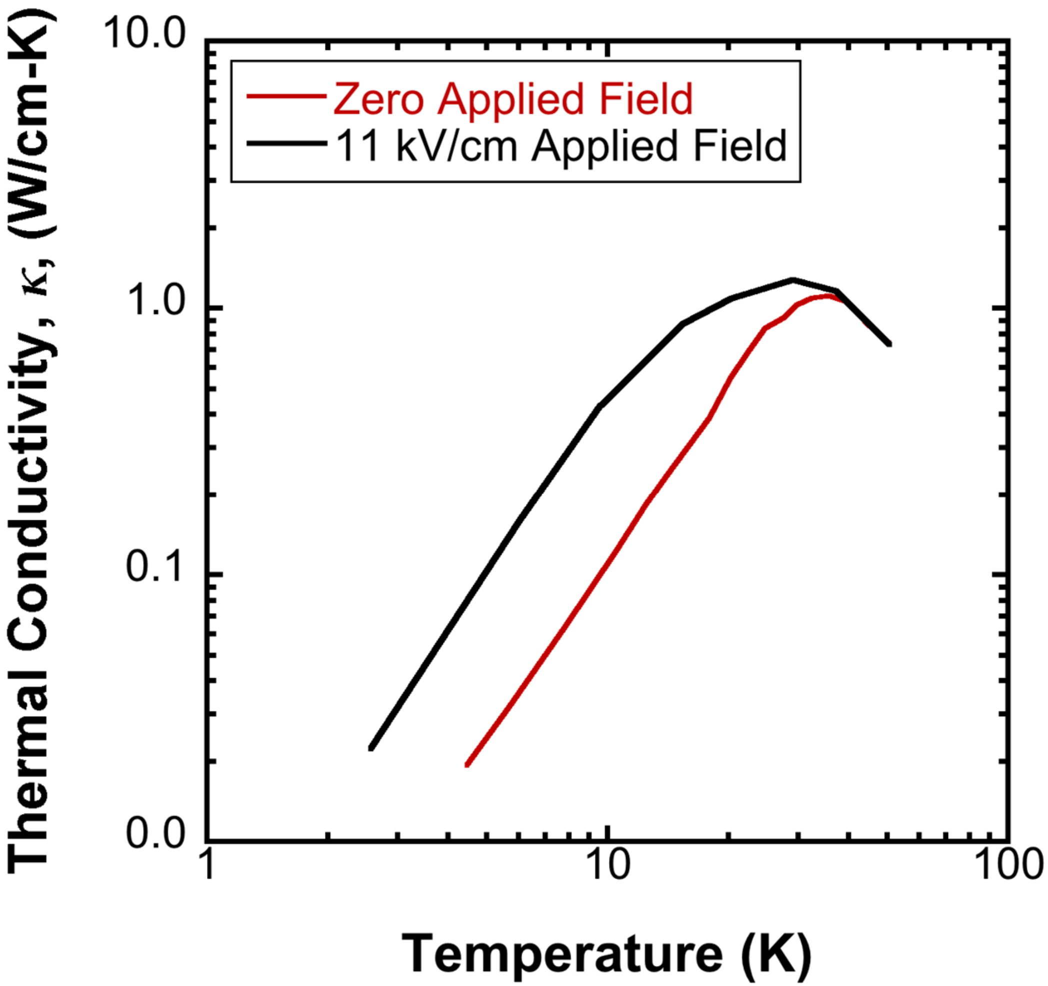
- Strain and orientation changes across coherent interfaces are known to affect thermal conduction
- These two features both exist at ferroelastic domain walls
- We would therefore anticipate that ***domain boundaries can scatter phonons***



Coherent Interfaces: Domain Boundaries

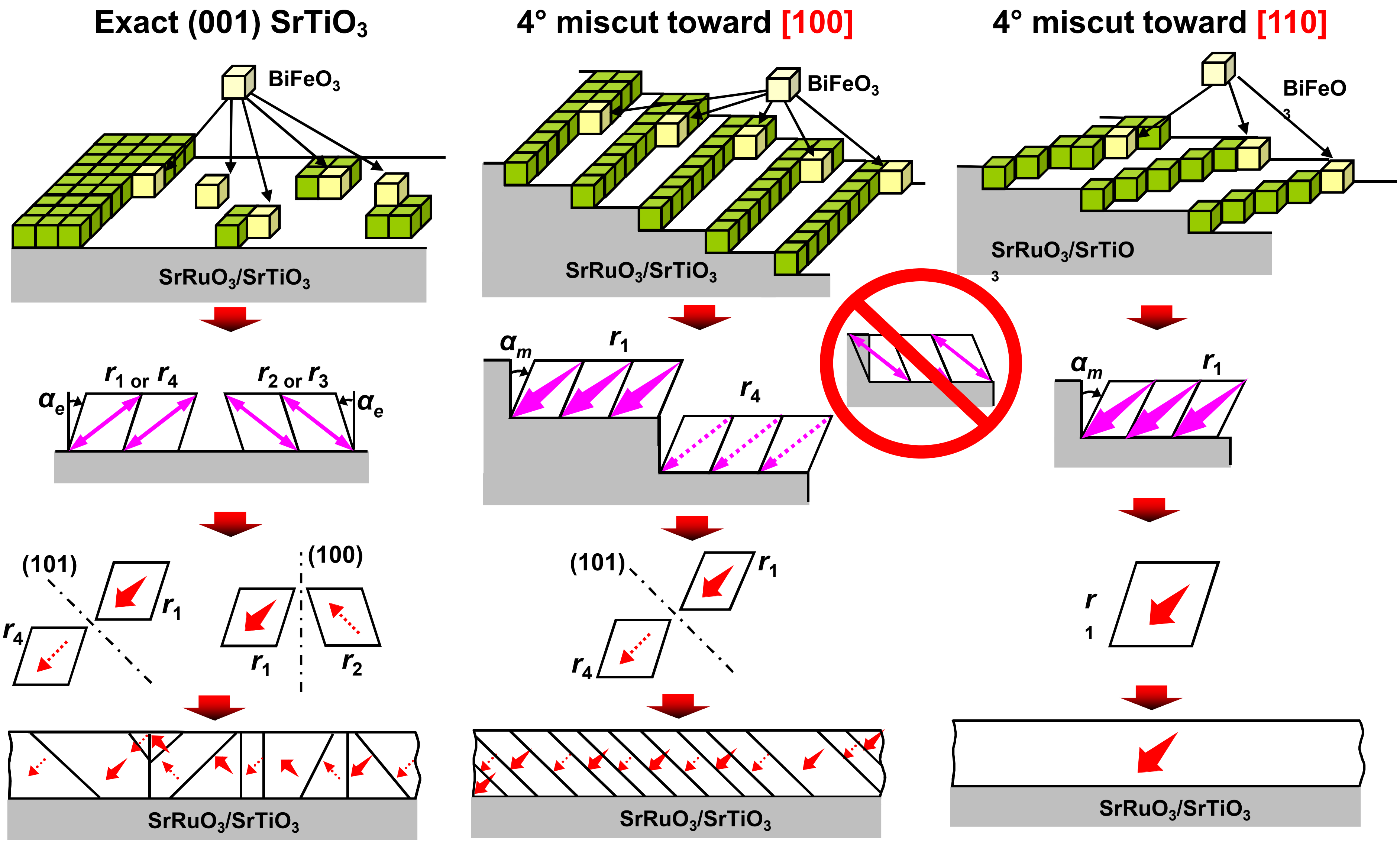
- Strain and orientation changes across coherent interfaces are known to affect thermal conduction
- These two features both exist at ferroelastic domain walls
- We would therefore anticipate that ***domain boundaries can scatter phonons***
- What about domains in thin films?

$BaTiO_3$ Single Crystal Thermal Conductivity*

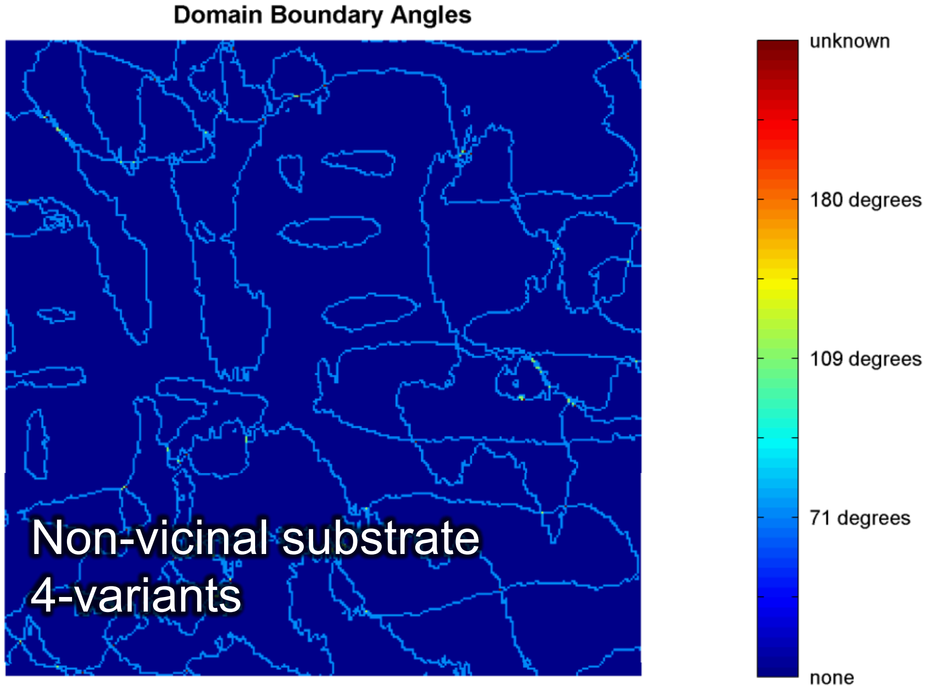


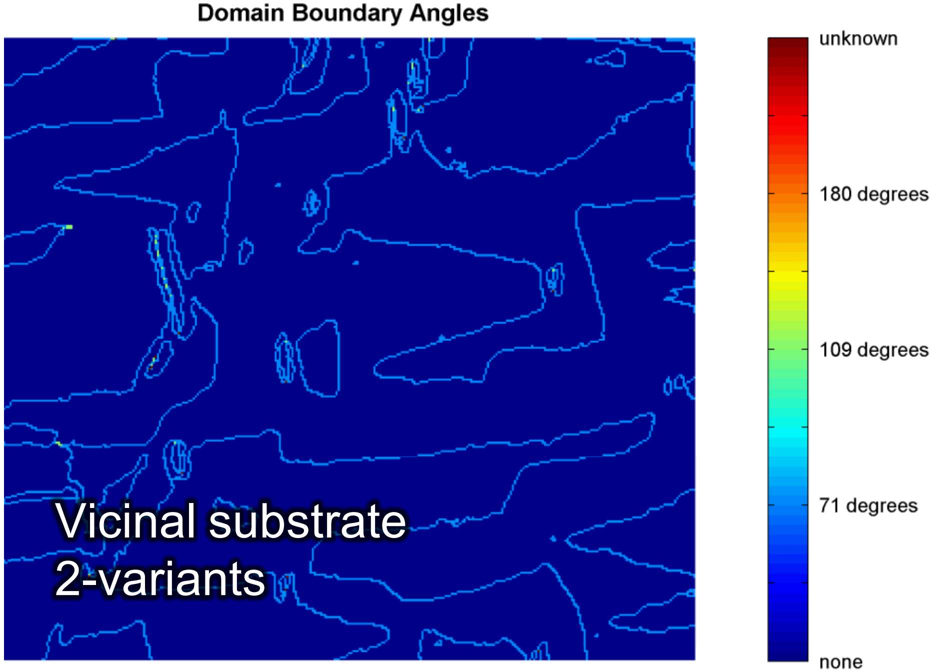
*Data adapted from: Mante and Volger, *Physica*, 1971

Substrate Vicinality to Engineer Domains



Domain boundary quantification





- 30 nm thick $BiFeO_3$ grown on non-vicinal and vicinal (001)-oriented $SrTiO_3$ substrates via reactive molecular-beam epitaxy
- Vector-Resolved PFM Characterization
  - Virtually all 71° domain walls
  - 4-variant: 16 μm domain wall/μm^2
  - 2-variant: 11 μm domain wall/μm^2
  - 1-variant: no observable domain walls

P.E. Hopkins, and J.F. Ihlefeld, *et al. Appl. Phys. Lett.* **102,** 121903 (2013)

Thermal Conductivity of $BiFeO_3$

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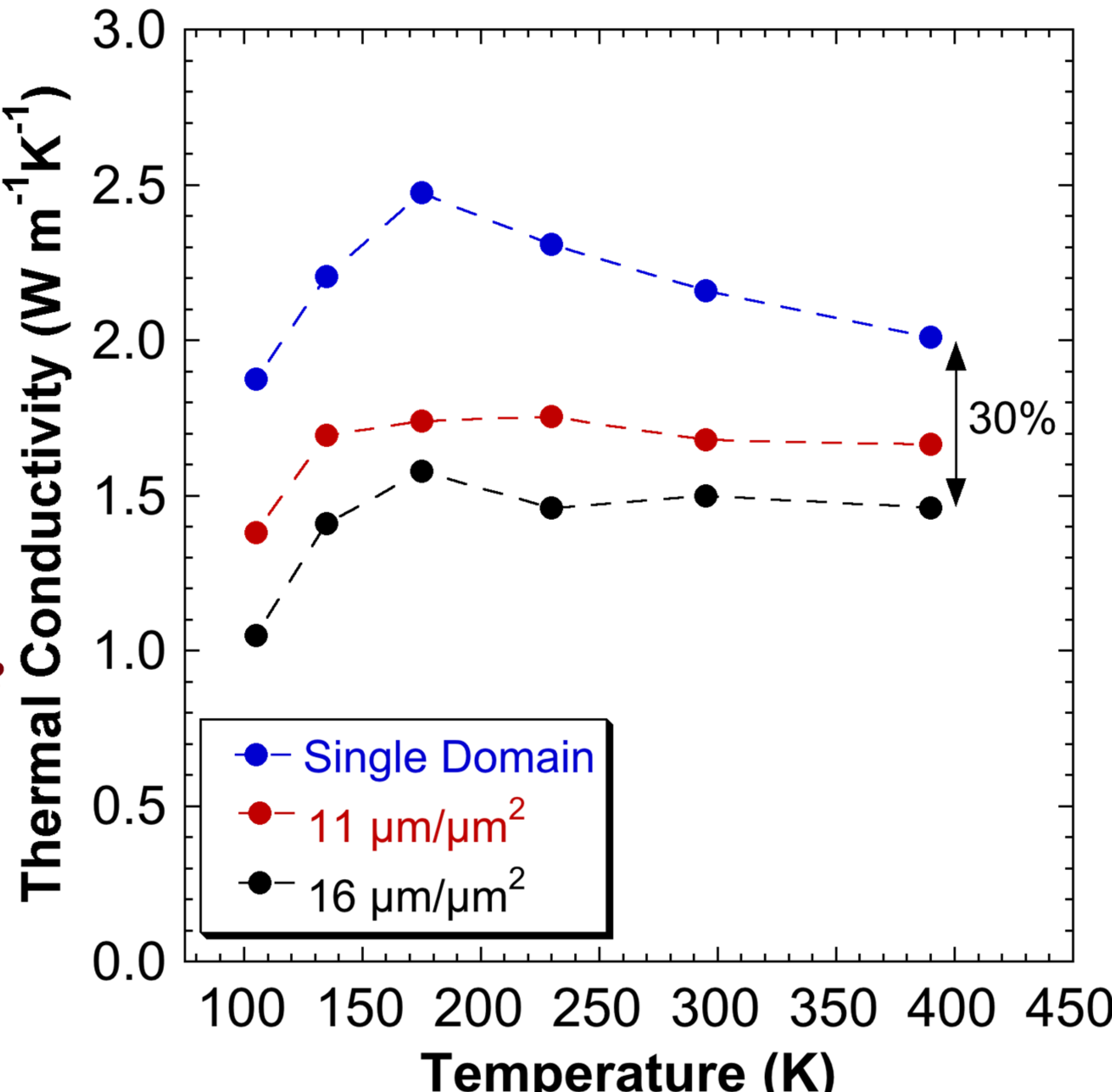
- Effective thermal conductivities of $BiFeO_3$ <2.5 W/m-K
- Presence of domain walls reduces κ by ~30%.
- ***Domain walls appear to be scattering phonons to at least 400 K***



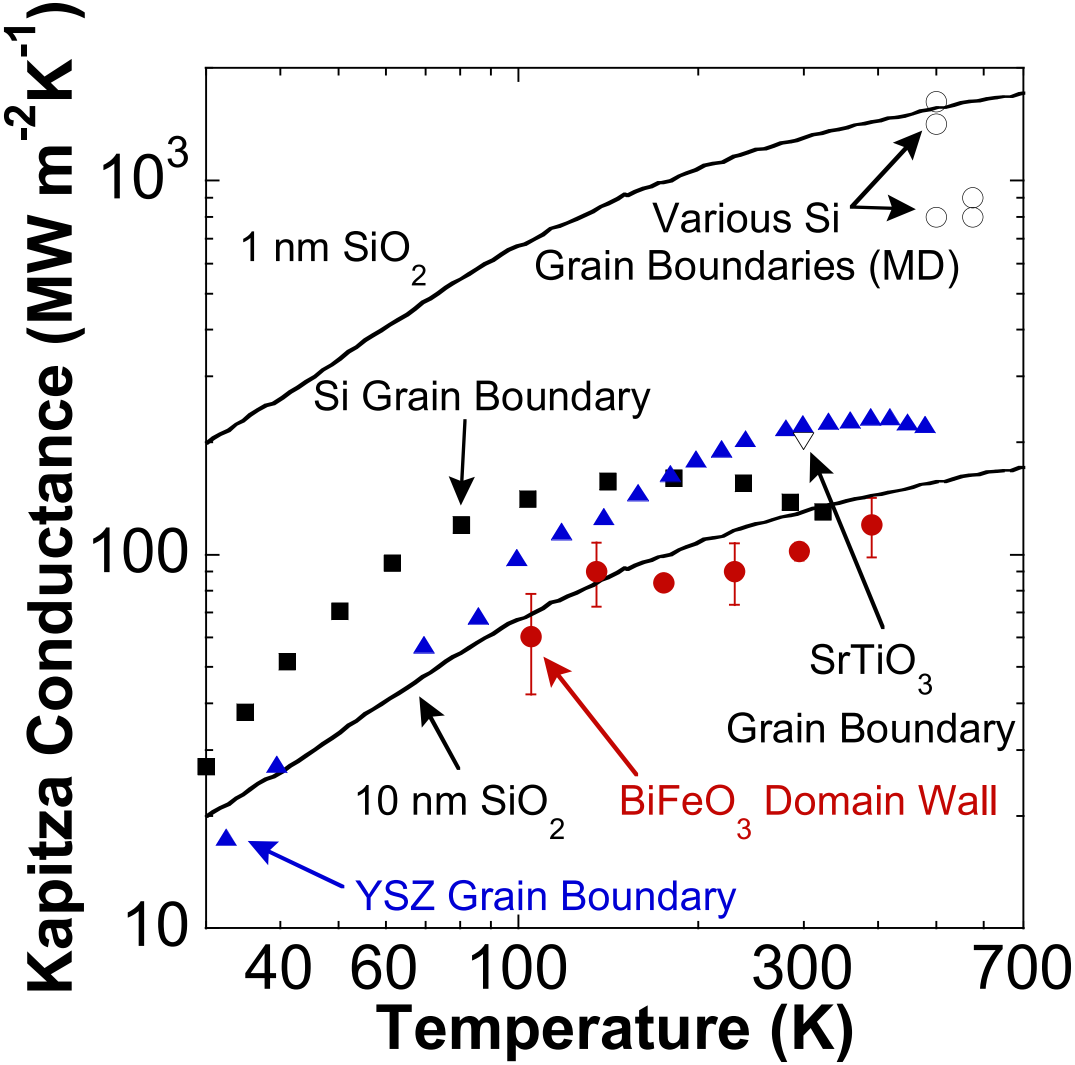
P.E. Hopkins, and J.F. Ihlefeld, *et al. Appl. Phys. Lett.* **102,** 121903 (2013)

Domain Wall Kapitza Conductance

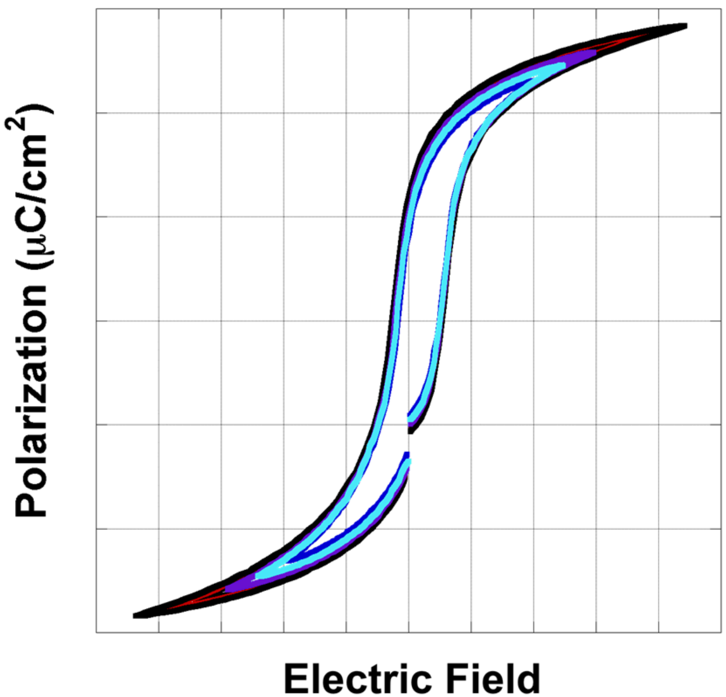
- Domain wall Kapitza conductance calculated from thermal conductivity data:

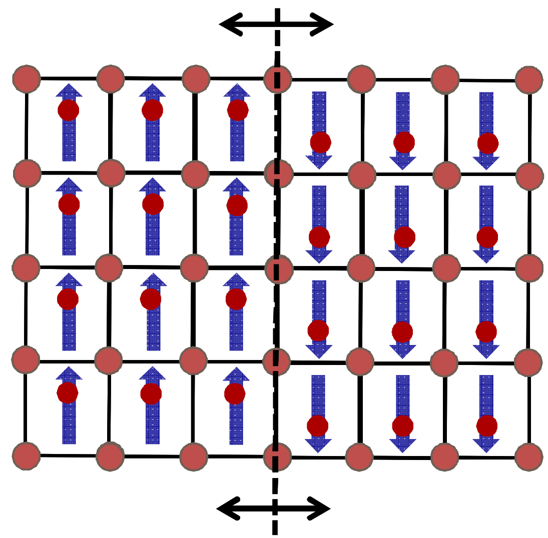
$$h_k = \frac{\kappa_0}{d\left(\frac{\kappa_0}{\kappa} - 1\right)}$$

- ***71° $BiFeO_3$ domain walls have thermal resistances greater than grain boundaries in similar materials***

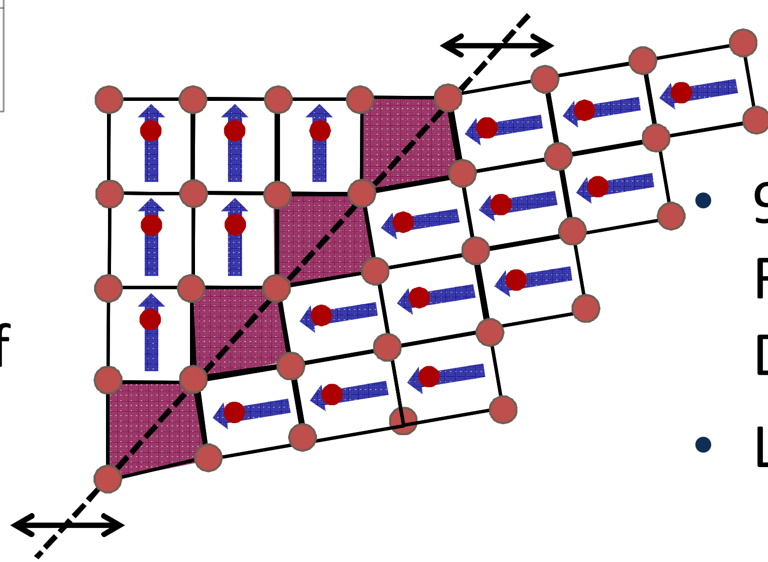


Domain Walls and Switchable Polarization





- 180° Ferroelectric Domain Wall
- Nominally no Strain

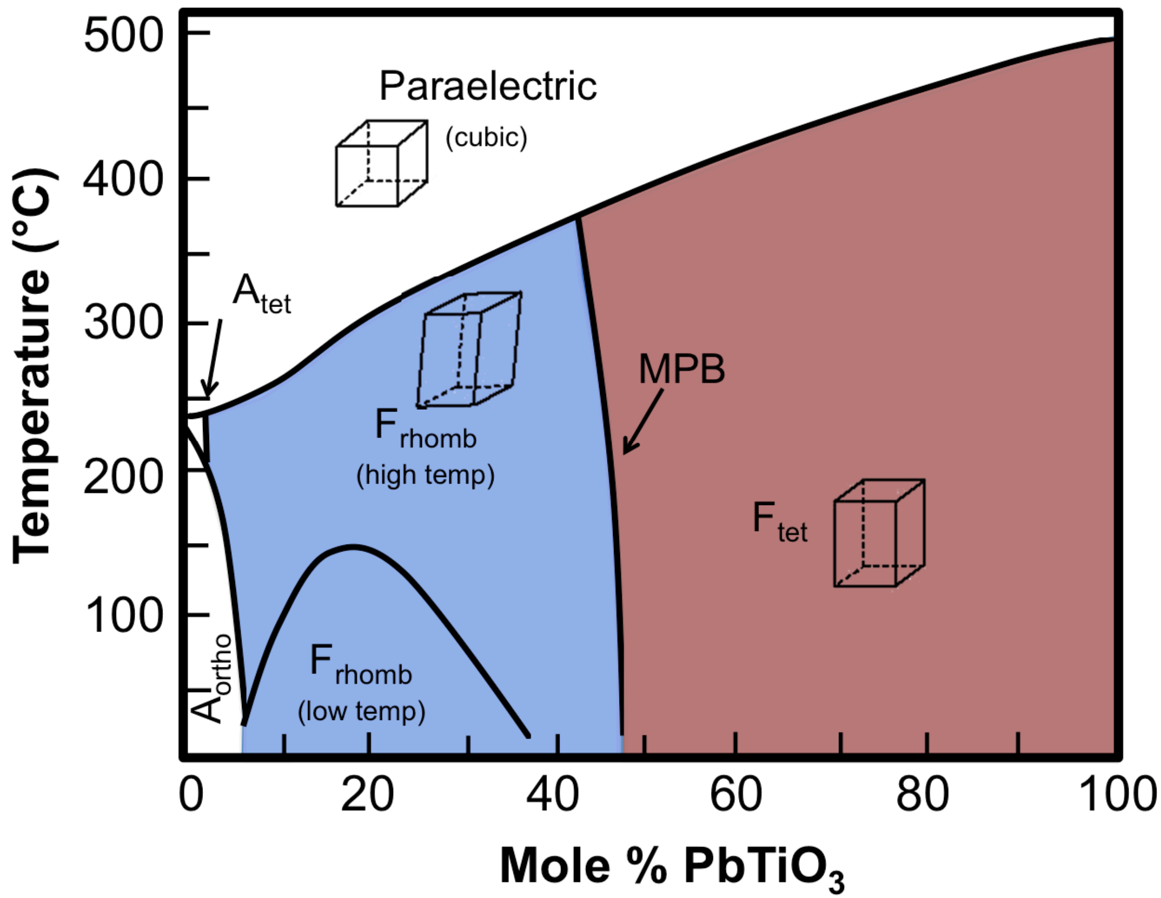


- 90° Ferroelastic Domain Wall
- Large Strain

Polarization switching generally requires motion of a ferroelectric/ferroelastic boundary

PZT to Test for Tunable Thermal Conductivity

- Relatively easy to make high quality thin films
- Rich-phase diagram provides opportunities to tune symmetry, domain wall types, and domain wall strain



SNL IMO $Pb(Zr,Ti)O_3$ CSD Film Preparation

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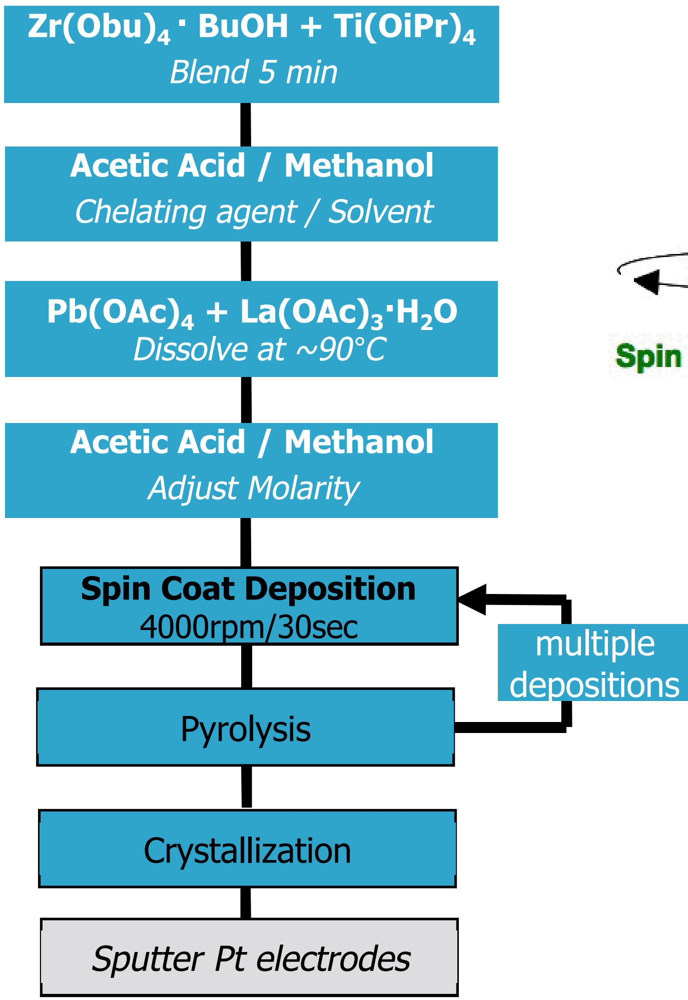
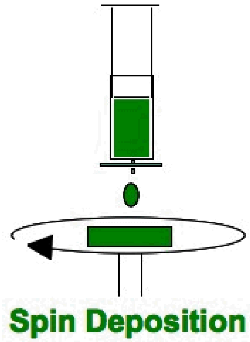
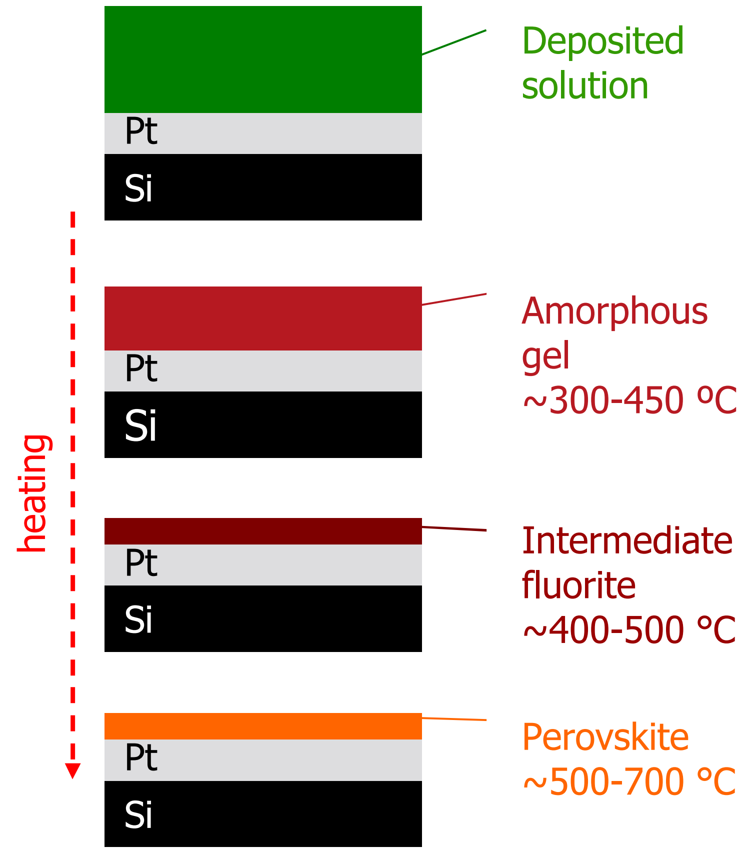


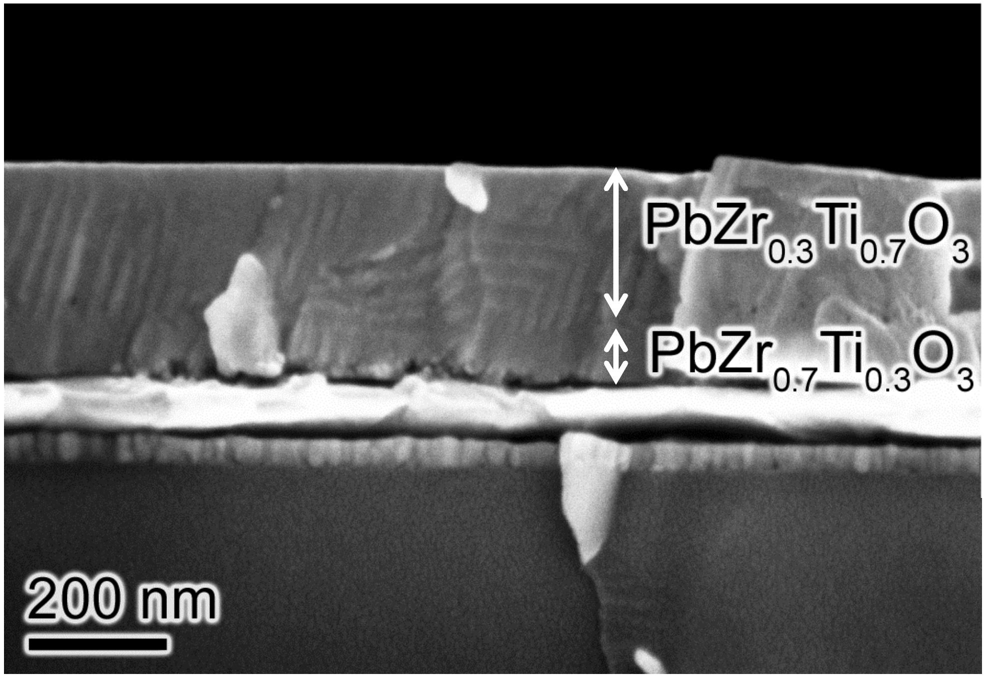


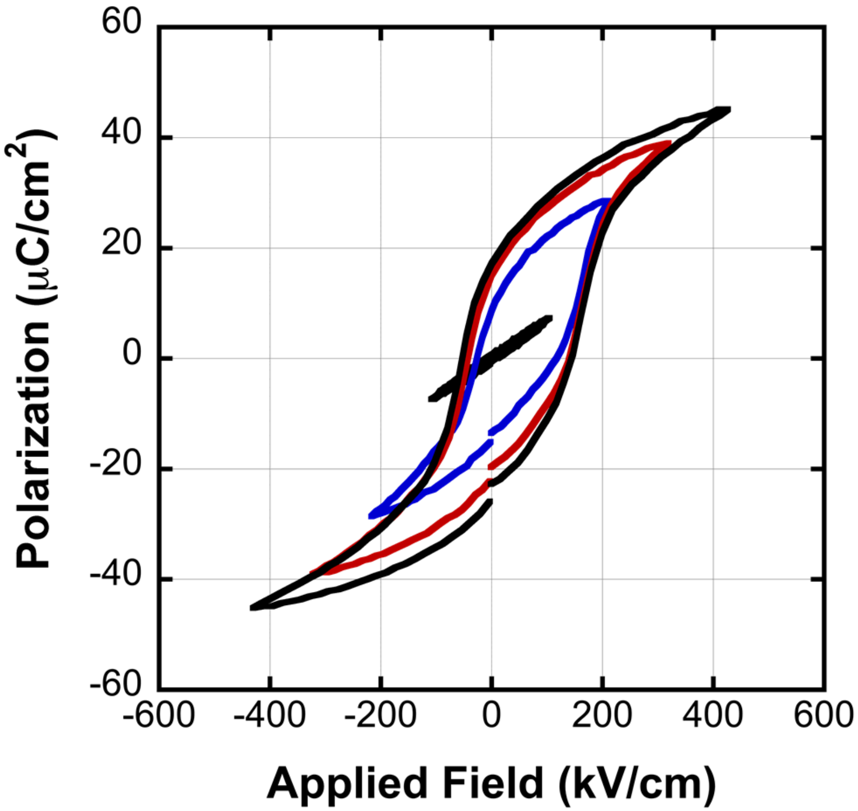


Assink & Schwartz *Chem. Mater.* (1993), G. Yi & M. Sayer. *J. Appl. Phys.* (1988)

Changing κ Requires Films with Mobile Domain Boundaries

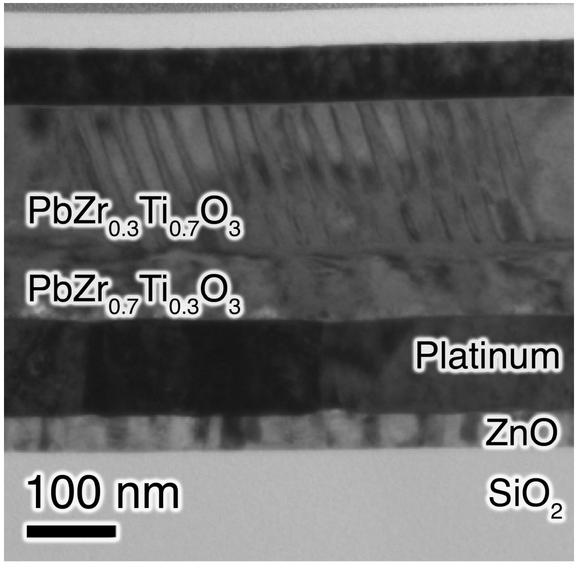
- PZT bilayers have been demonstrated to have highly mobile ferroelastic domain walls*
- Prepared bilayer films via CSD on $Pt/ZnO/SiO_2/Si$

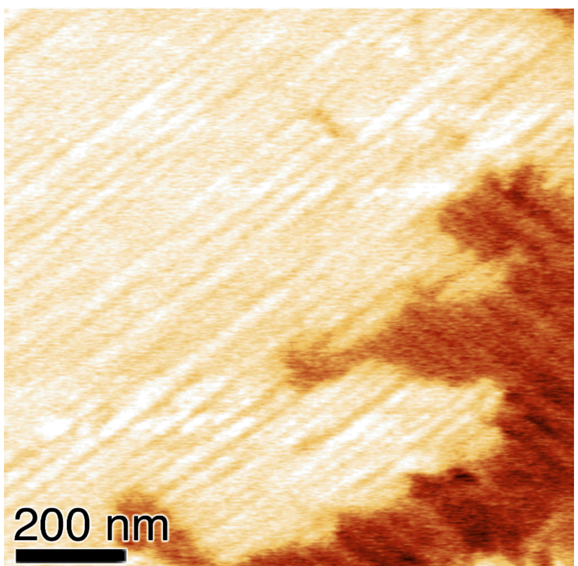




*Anbusathaiah and Nagarajan, *et al., Adv. Mater*. 21 3479 (2009)

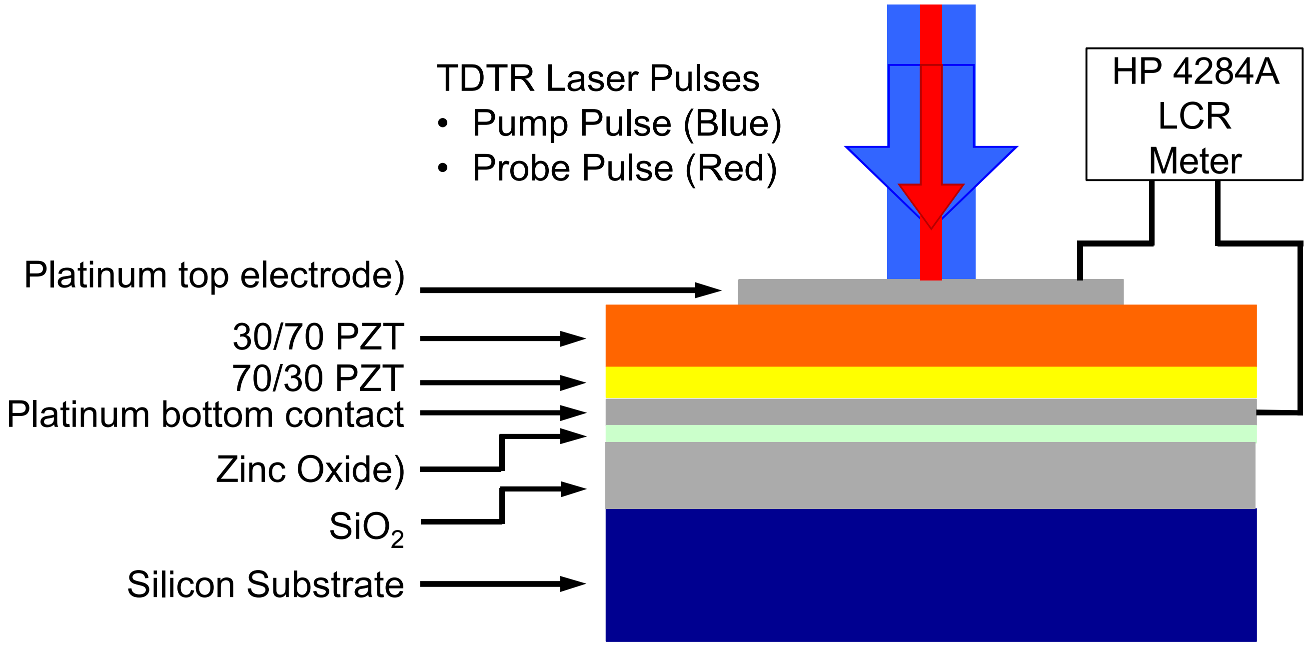
Domain Structure in PZT Bilayer Films





- Ferroelastic domain structure evident in both TEM and PFM images
- Twin structure consistent with twins on {110} planes – consistent with 90° domain walls
- Fine spacing of domain walls
  - TEM: 5-36 nm, 16.5 ± 6.6 nm average
  - PFM: 30.4 ± 3.3 nm average
- ***Fine spacing of walls may allow scattering of phonons of longer wavelengths***

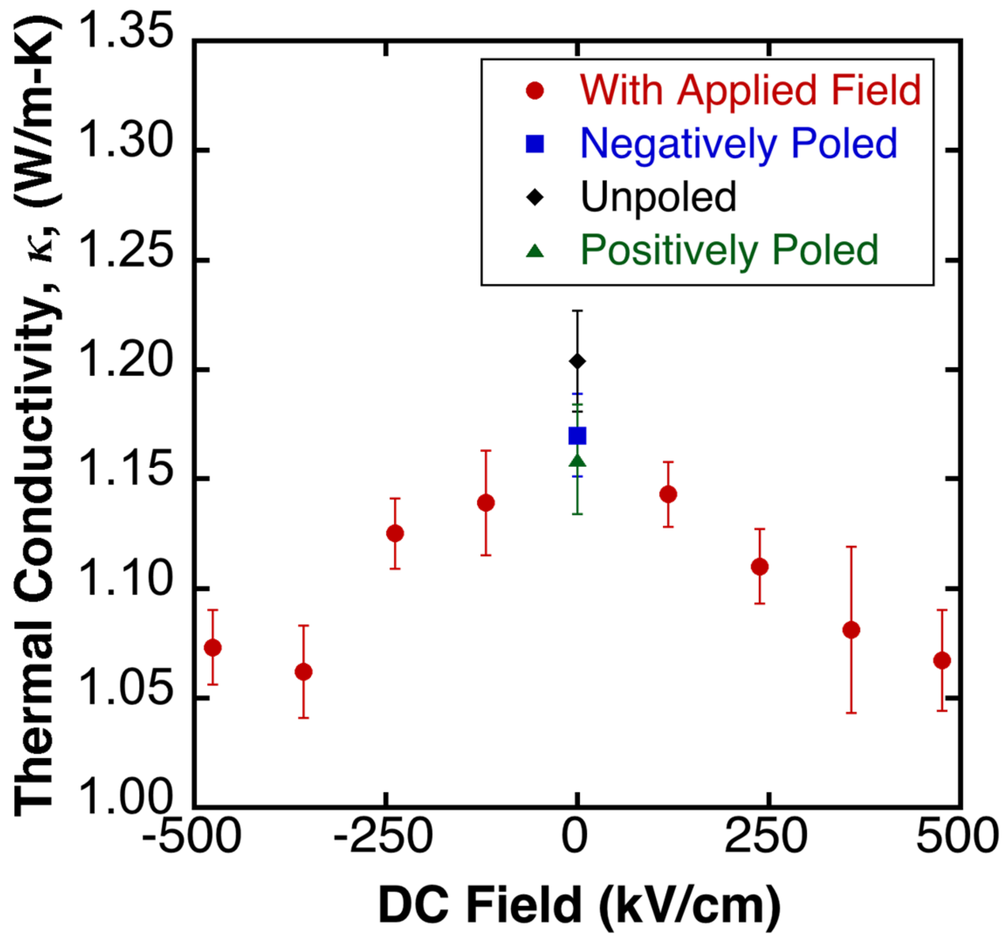
Thermal Conductivity Measurement Under Applied Field



- Platinum electrode used as TDTR transducer and electrical contact
- DC Bias applied in cross-plane configuration
- “Health” of the PZT monitored by capacitance and loss tangent while under measurement

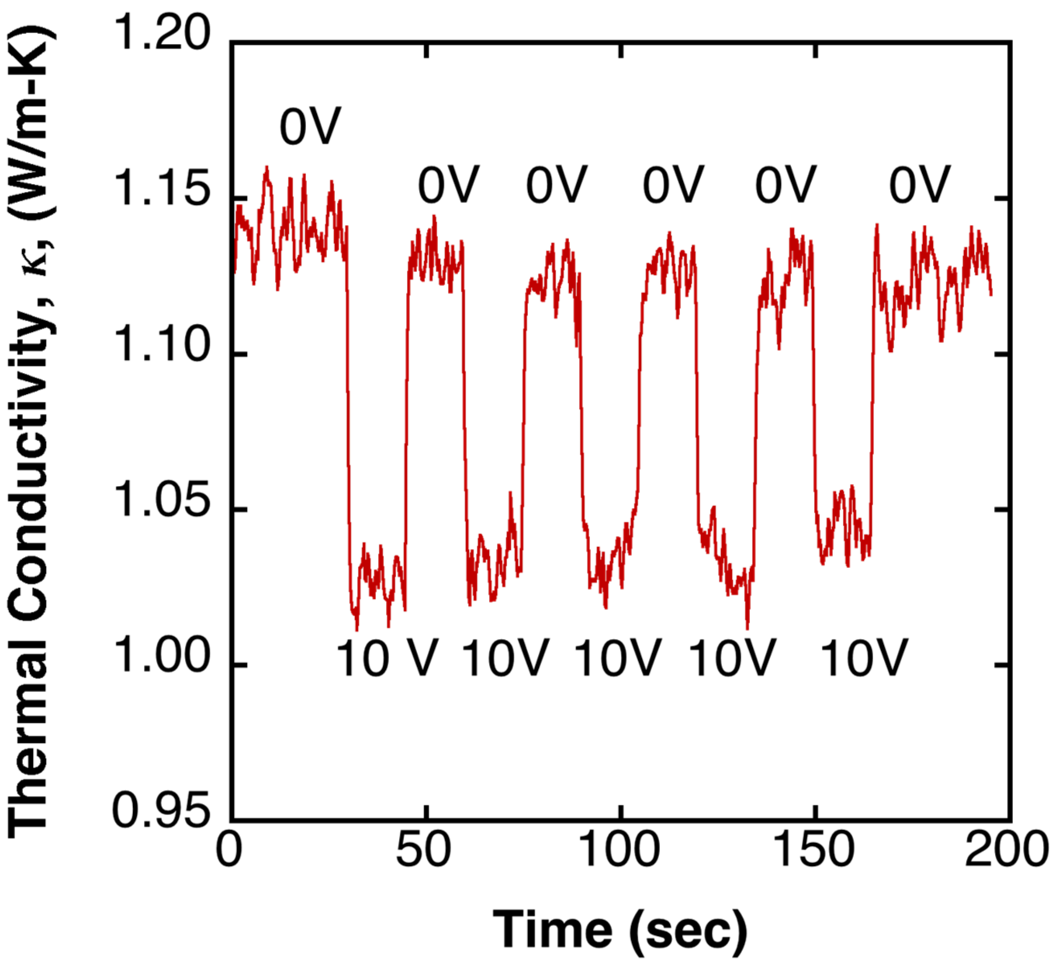
Field-dependence of thermal conductivity in PZT

- Measured thermal conductivity with TDTR while applying a bias at room temperature
  - Used LCR meter to ensure loss was not increasing with field
- Measurements take ~2-5 minutes with field applied
- ***Clearly observe a 12.5% decrease in thermal conductivity with applied field at <u>Room Temperature</u>***

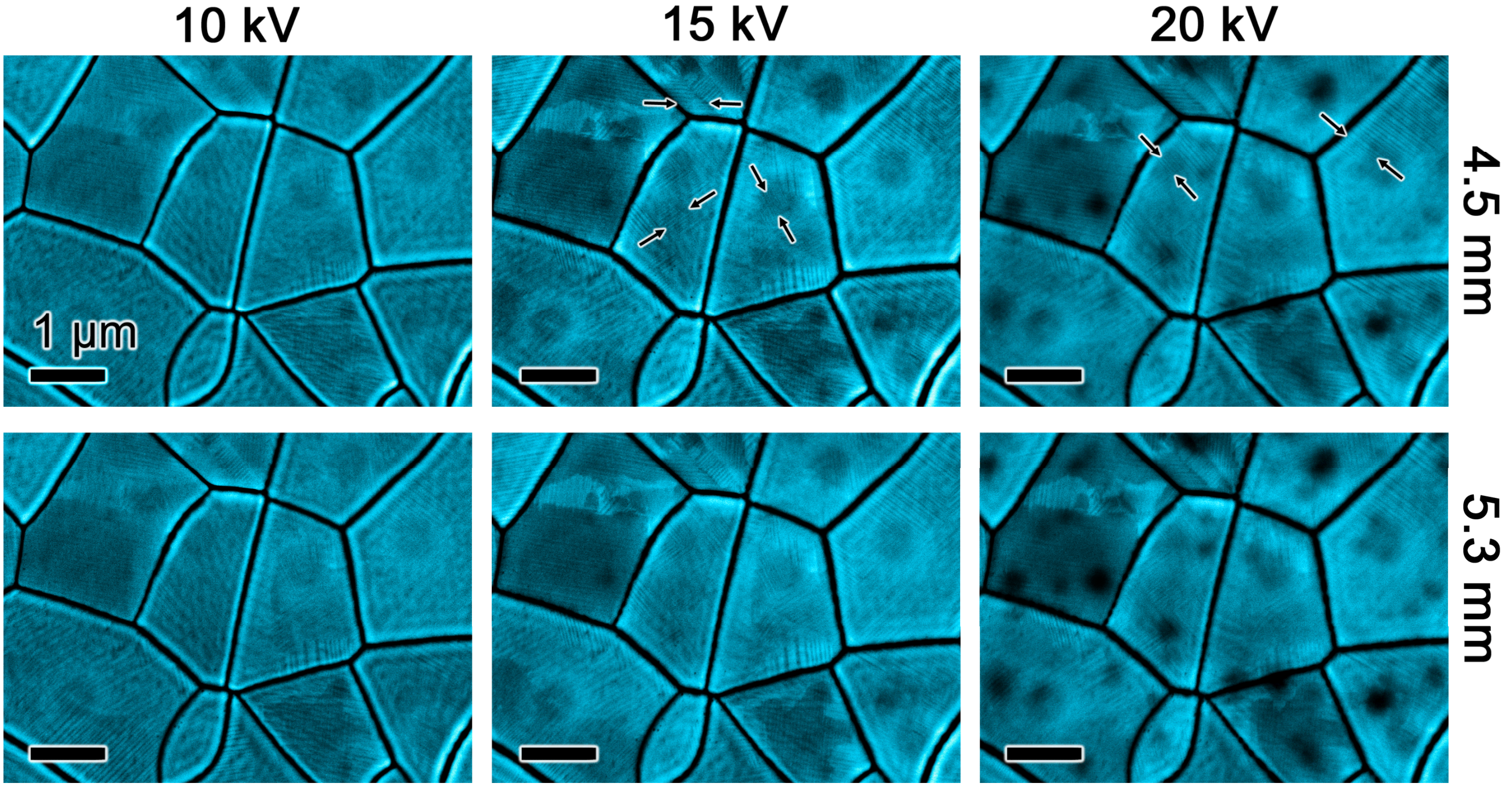


Field-dependence of thermal conductivity in PZT

- Thermal conductivity response is instantaneous
- Repeatable and recoverable response
  - Lose ~5-6% from unpoled to poled state
- ***A room temperature non-moving or non-phase transition associated thermal regulator***



Why does thermal conductivity decrease?



- Need method to observe domain structure while under field
- *In-situ* backscattered channeling contrast SEM enables observation of domain structure *during* application of applied voltage

Why does thermal conductivity decrease?

- Need method to observe domain structure while under field
- *In-situ* channeling contrast SEM may enable observation of domain structure *during* application of applied voltage
  - 3 nm thick Pt electrode used to allow electron transparency

Why does thermal conductivity decrease?

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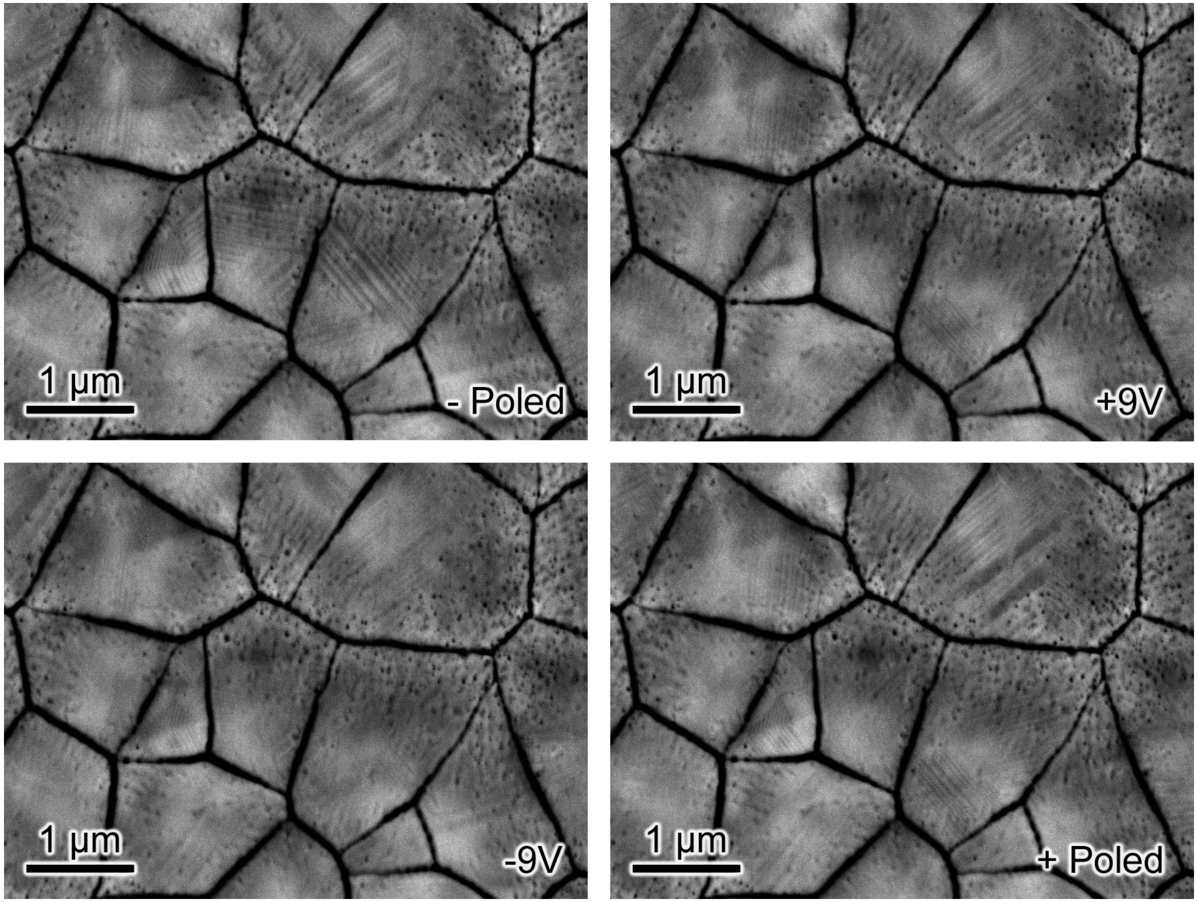
- *In-situ* channeling contrast SEM enables observation of domain structure *during* application of applied voltage
  - 3 nm thick Pt electrode used to allow electron transparency
- Domain structure becomes ***more*** complex under applied fields*



*Ivry, *et al.*, *Phys. Rev. B.* **81**, 174118 (2010)

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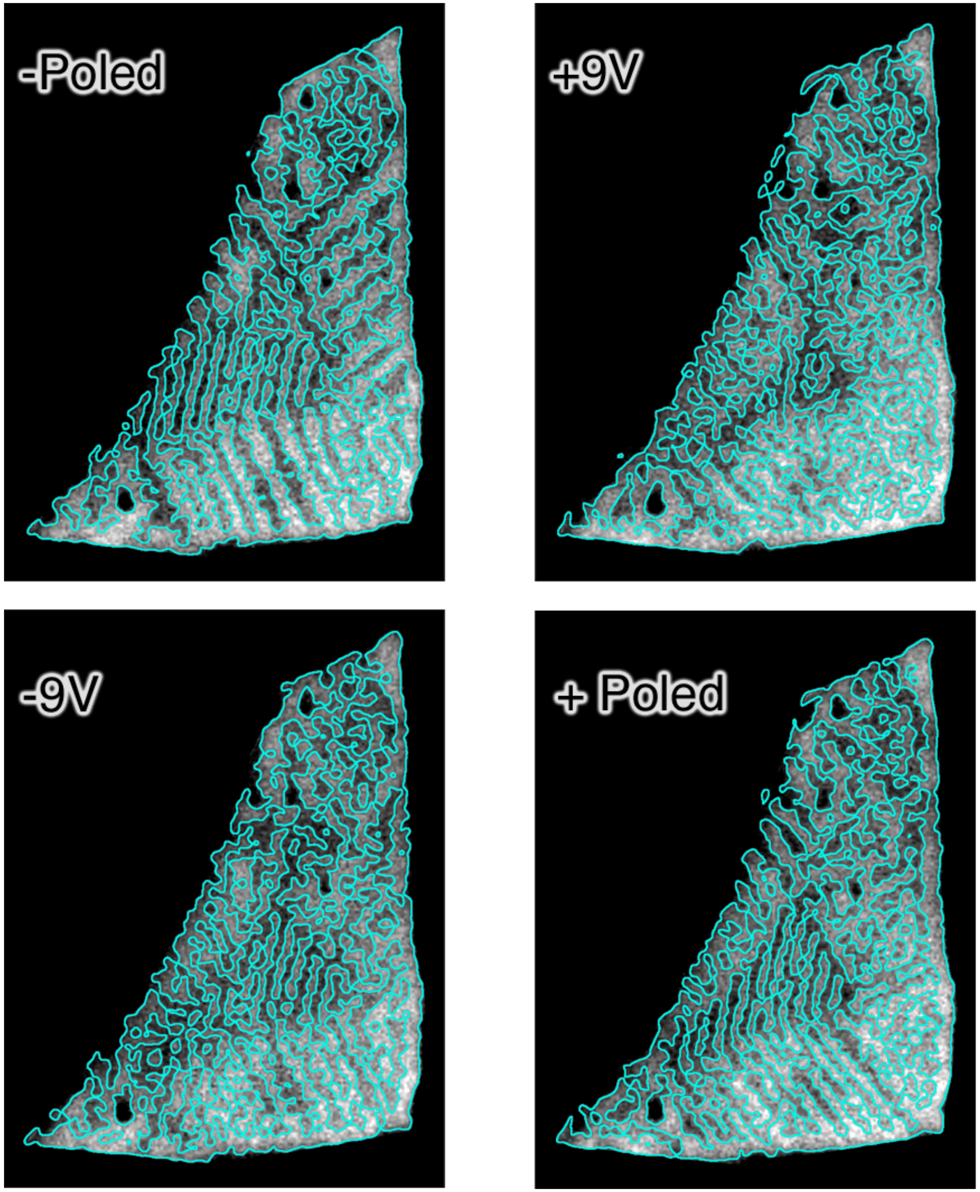

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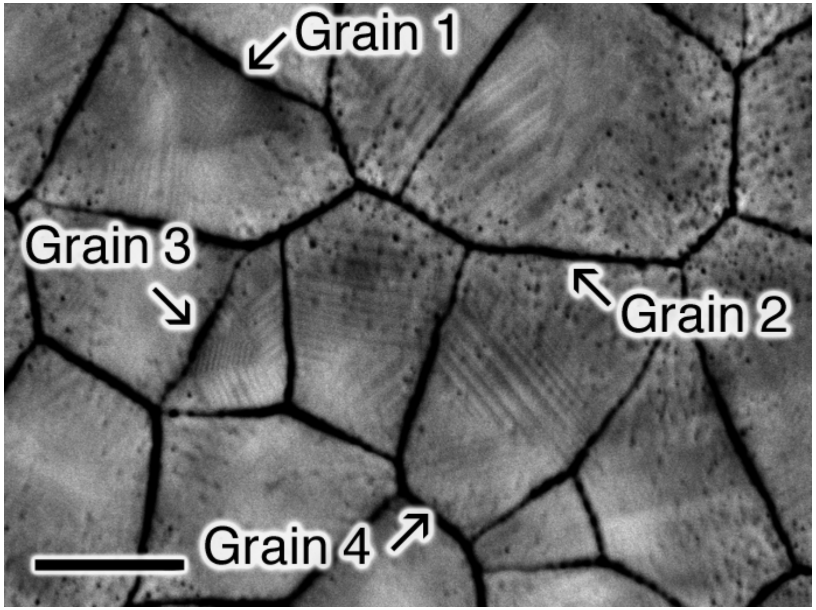
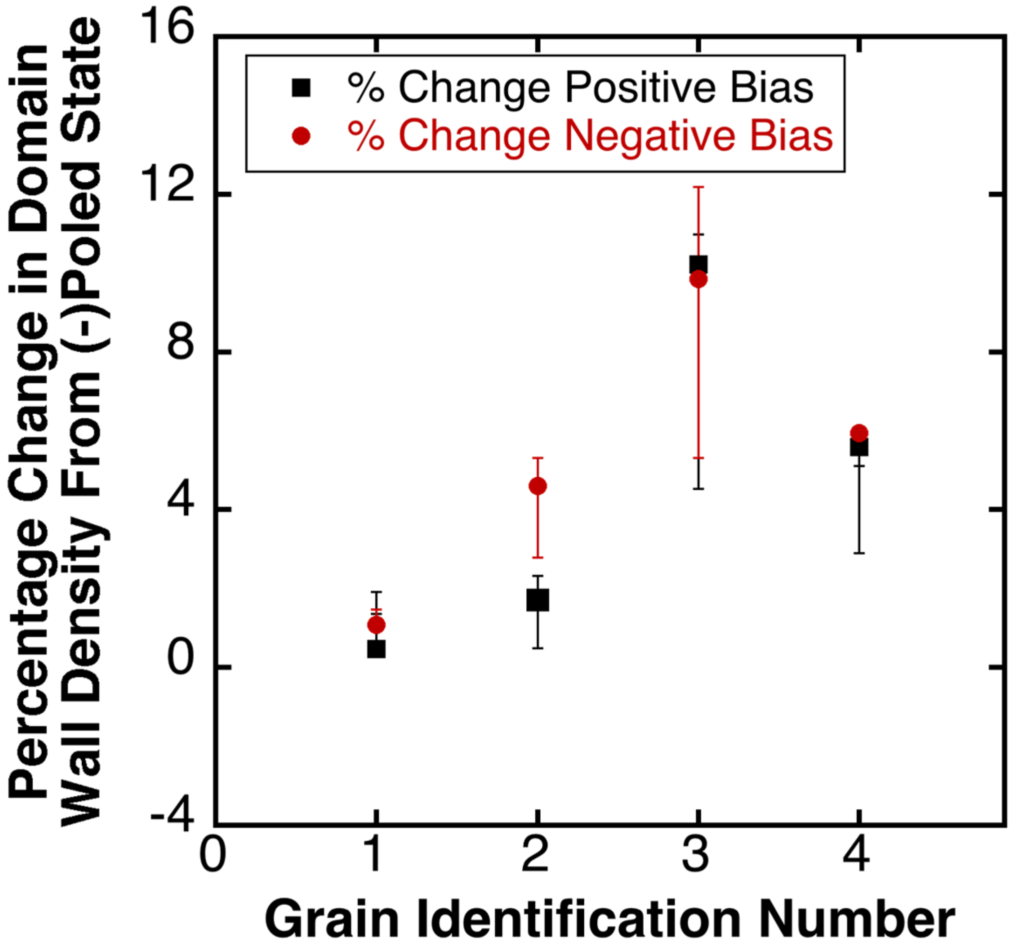
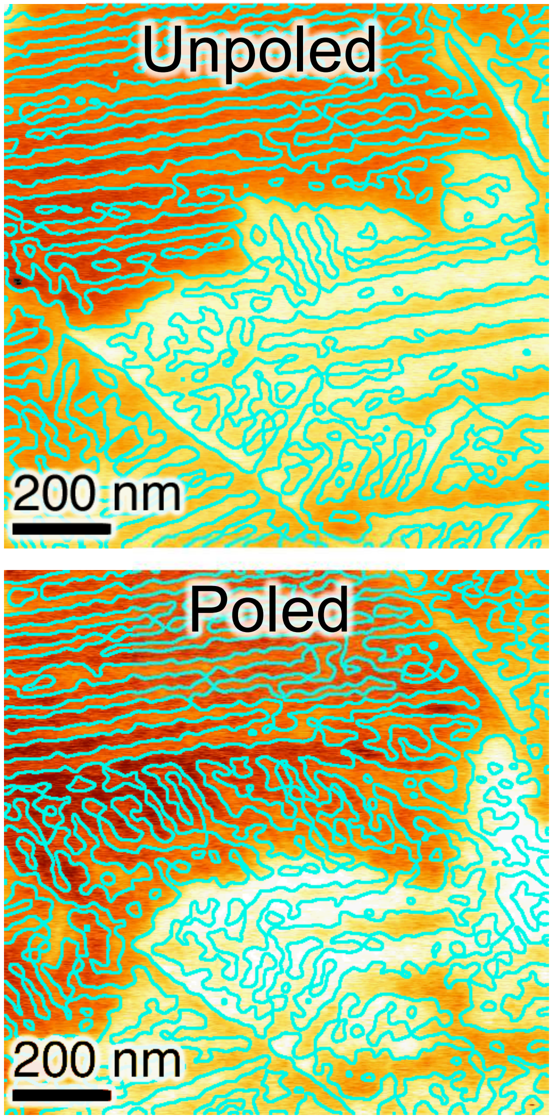
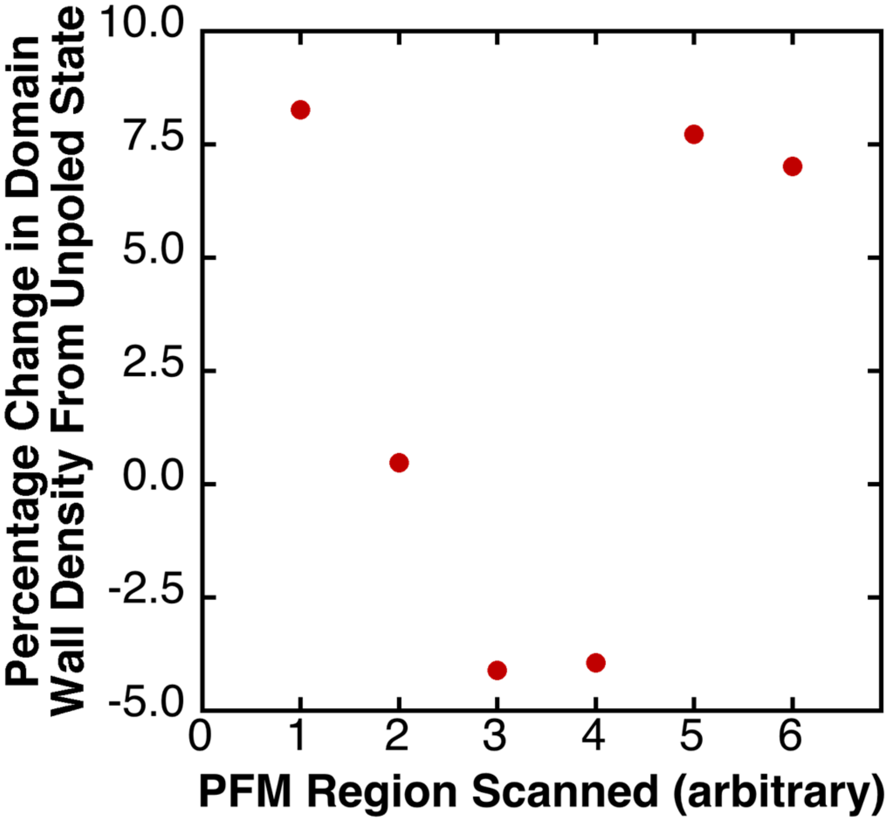




All grains with observable domain structure changes under field show increases in domain density

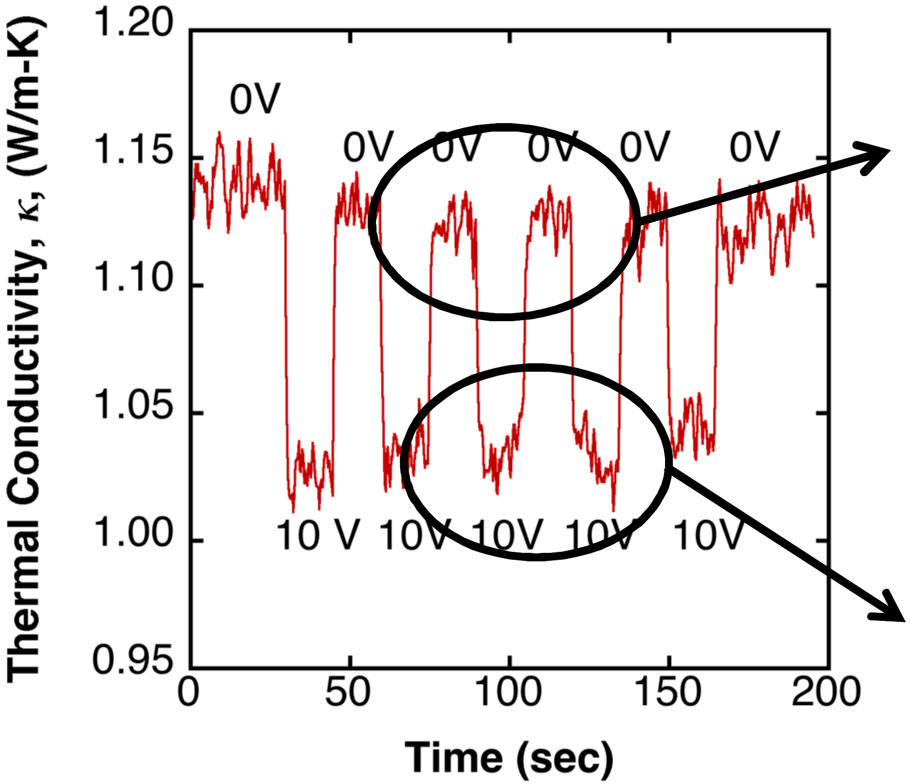
Why does thermal conductivity decrease?

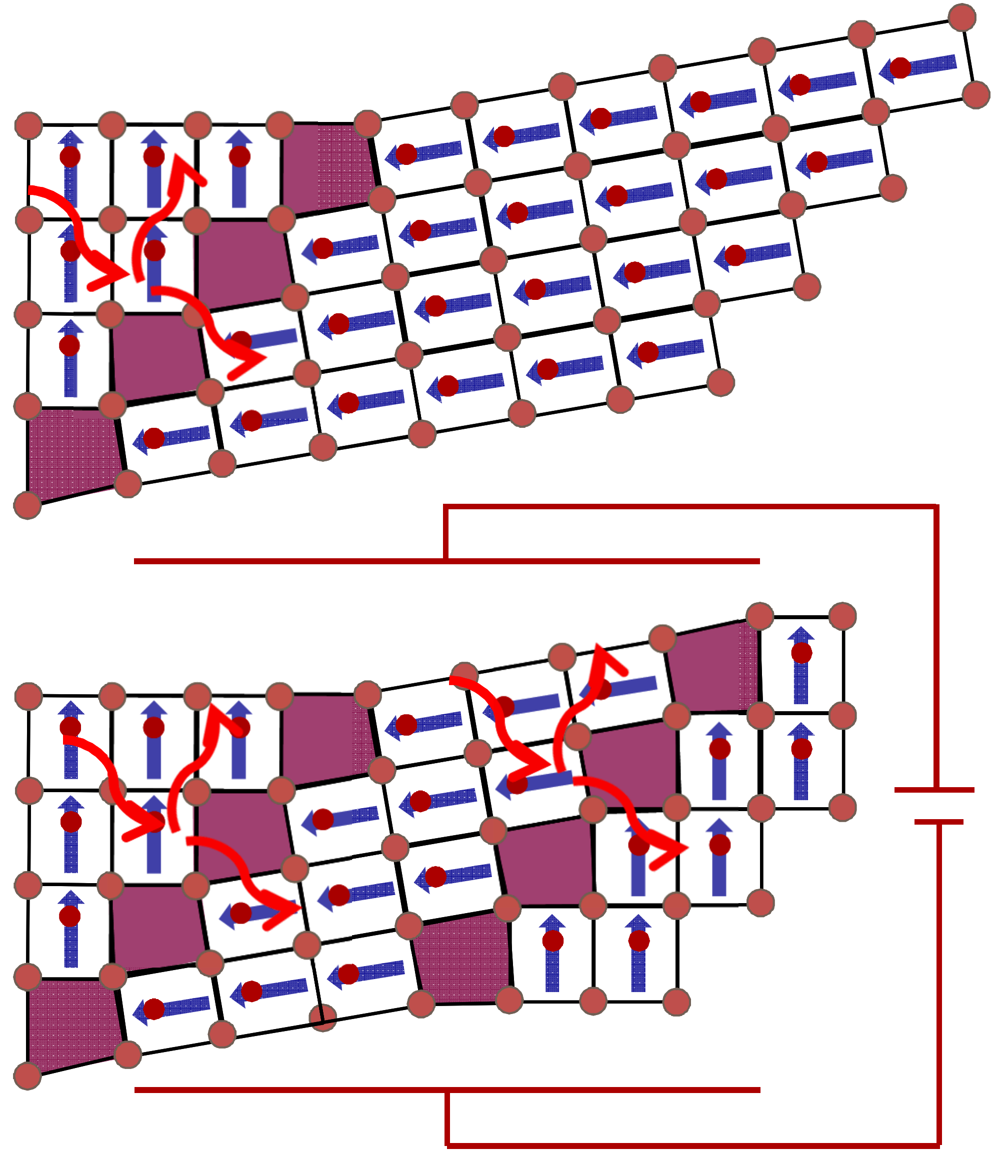




- Domain wall density changes between unpoled and poled states varied depending on region
- ***Mostly see an increase in domain density***

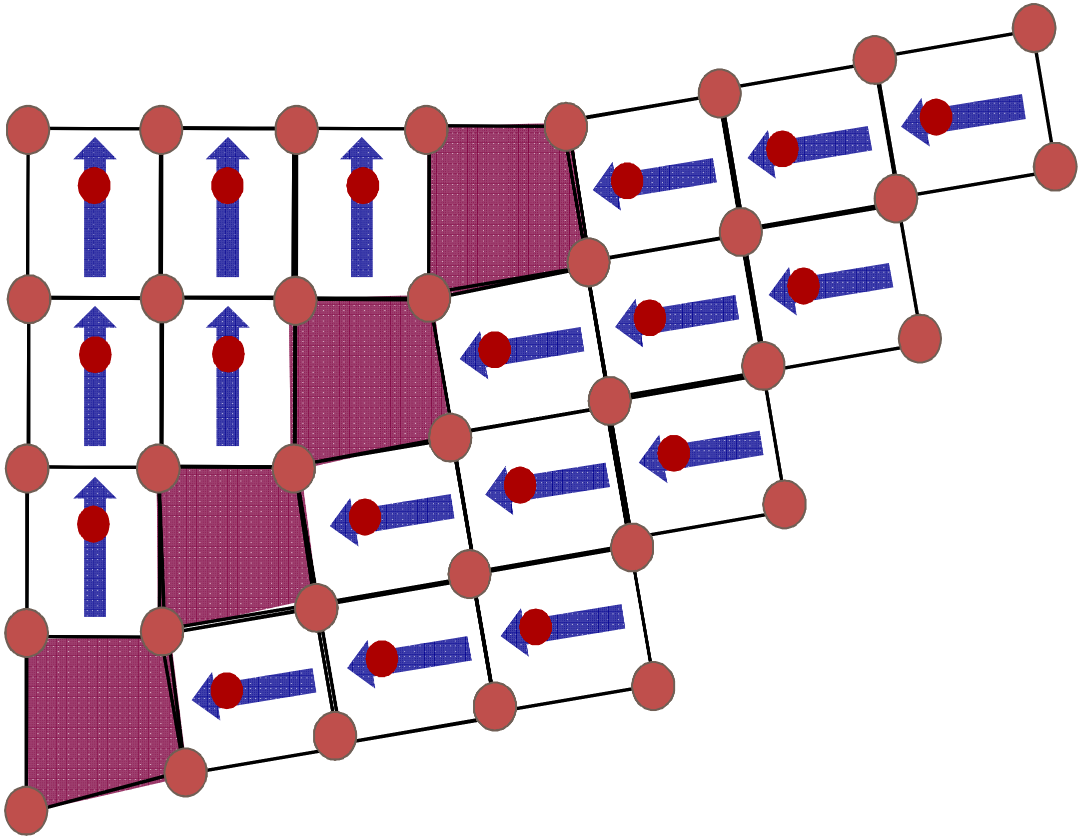
Domain Wall Density Increase is Responsible for κ Decrease





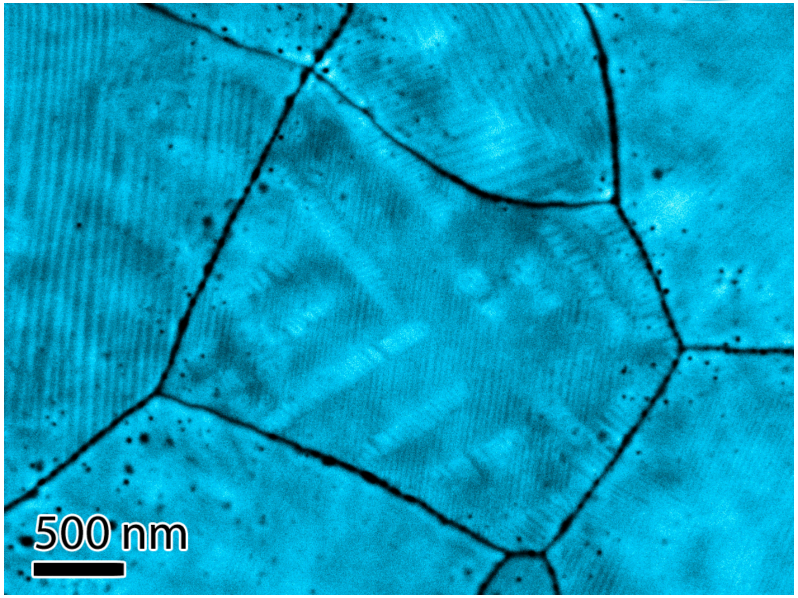
What is the Mechanism for Phonon Scattering?

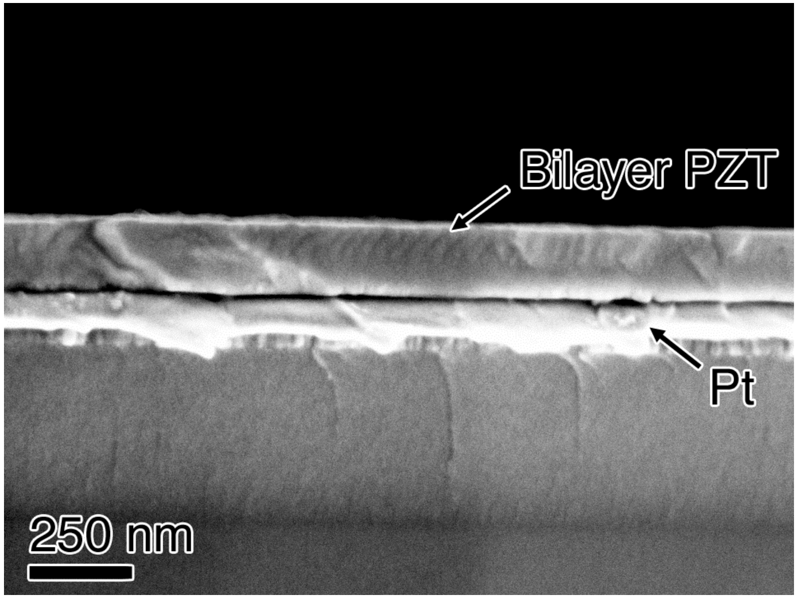
- Interface scattering due to translation vector change?
- Scattering due to strain field associated with domain wall?
- Temperature dependent data can help us determine the mechanism:
  - Interface scattering: Limited temperature dependence
  - Strain effects: Clear temperature dependence



Temperature Dependence of Thermal Conductivity Tunability

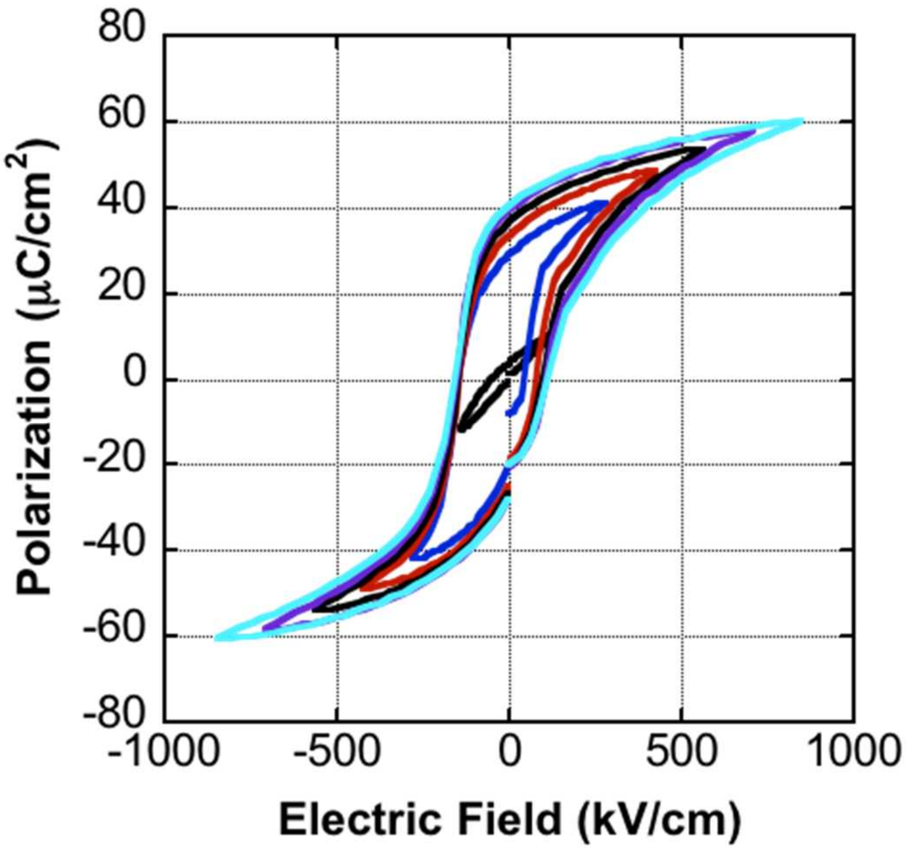
- 30/70 x 70/30 polycrystalline bilayer thin film
  - ~95nm 30/70 and ~77nm 70/30
- Ferroelastic domain structure again apparent in tetragonal 30/70 layer
  - Stripe domains most predominate
  - Domain bundles clearly evident in center grain
  - Plan-view: ~18 nm average spacing of domain walls

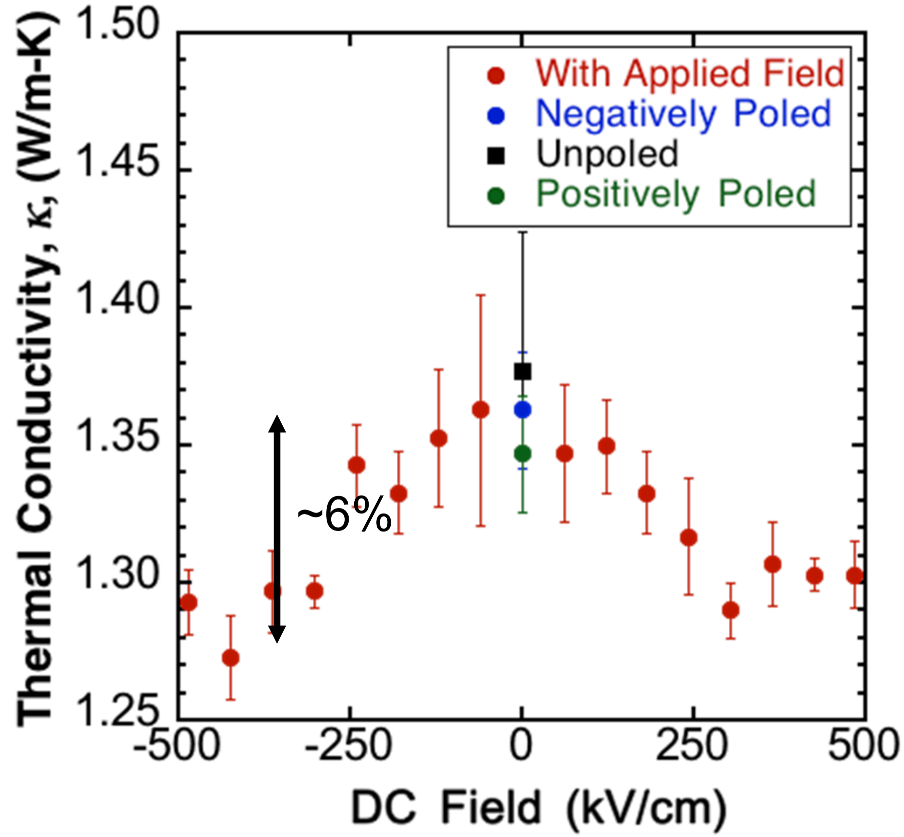




Temperature Dependence of Thermal Conductivity Tunability

- Clear room temperature polarization switching and thermal conductivity tuning





Temperature Dependence of Field Dependent Thermal Conductivity

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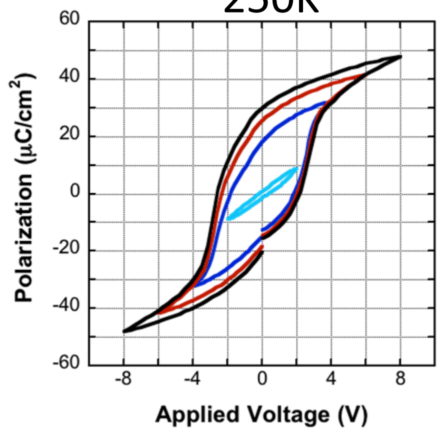
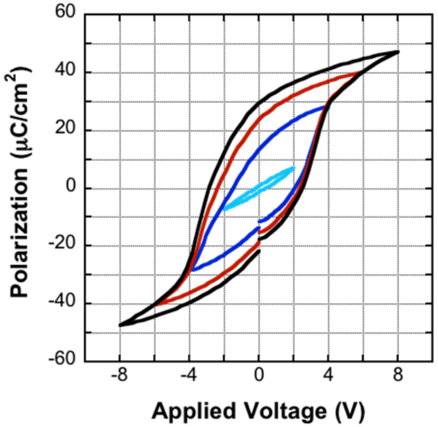
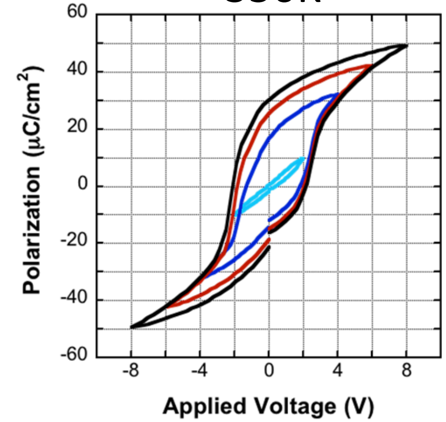
250K

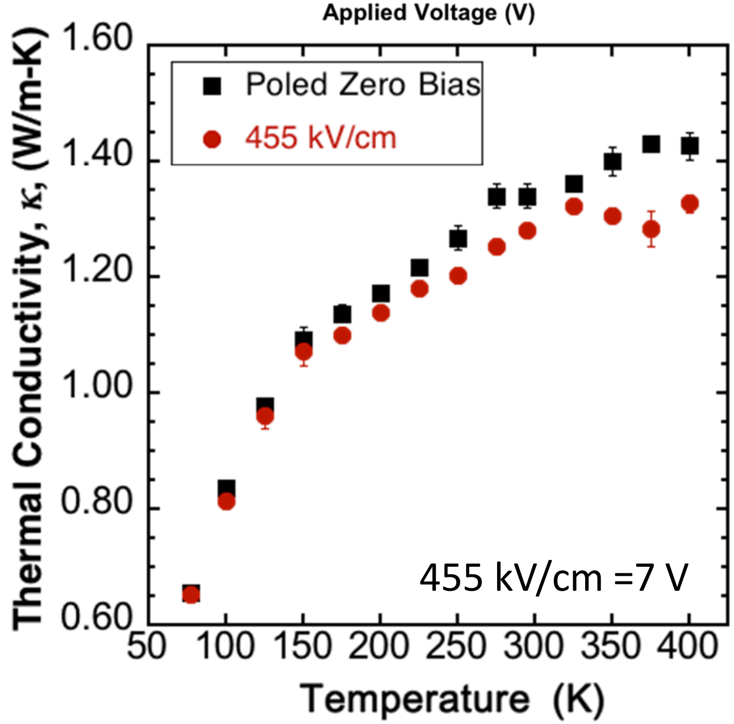


150K

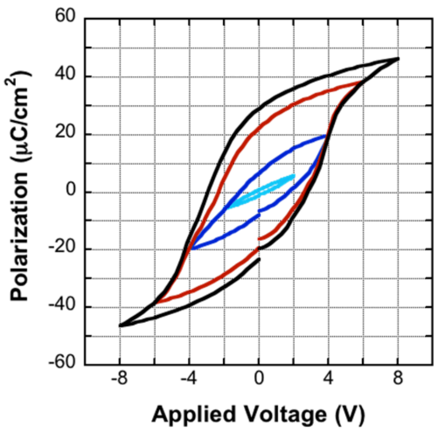


350K

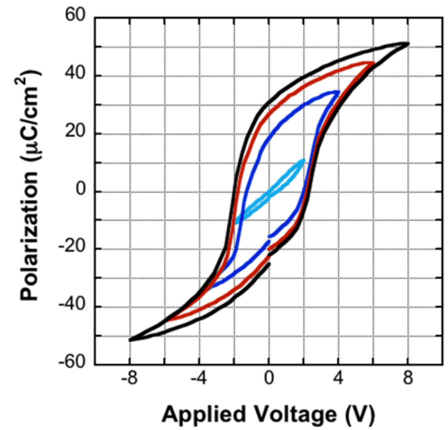




78K



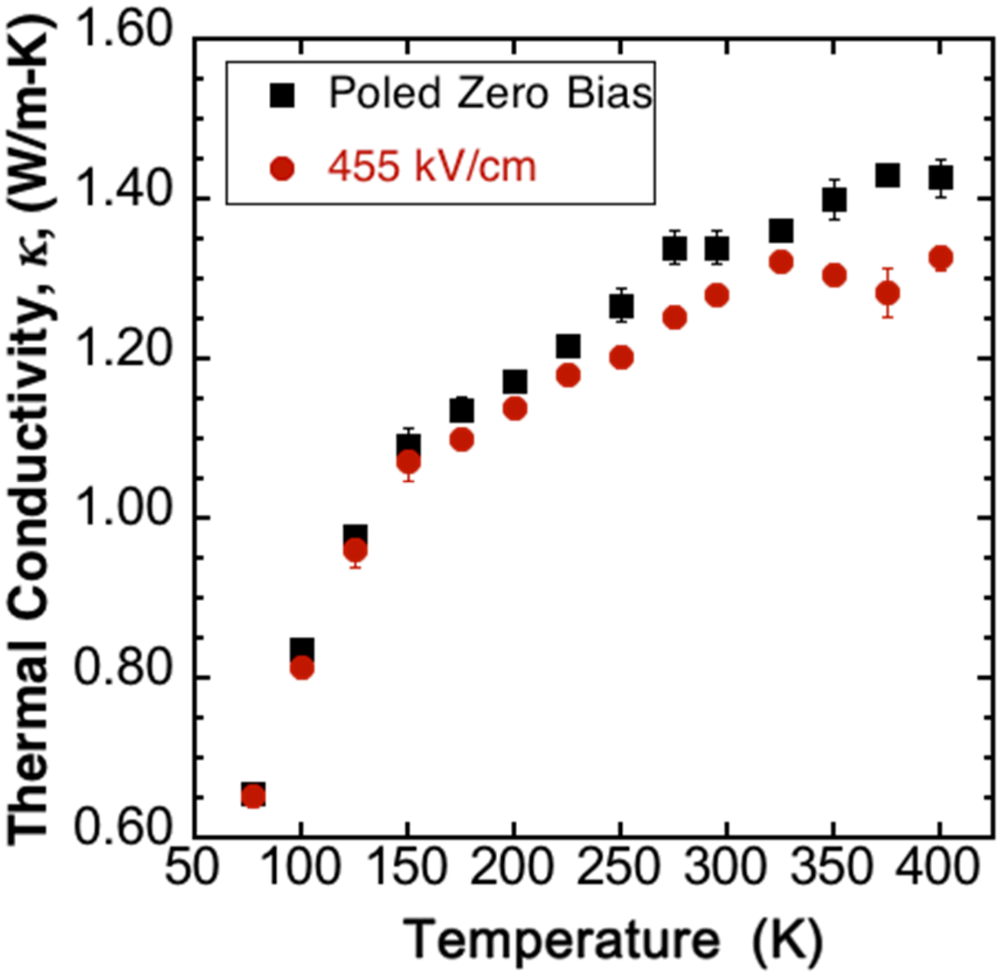
400K



Temperature Dependence of Field Dependent Thermal Conductivity

Sandia National Laboratories

- Difference between biased and poled states at >200 K
- Virtually no difference between biased and poled states at <200 K
- *If purely an interface effect, would see difference across entire temperature range*
- Response is more similar to that expected for strain effects (e.g. dislocation strain fields, etc.)
- ***Strain is the dominant contributor to domain boundary phonon scattering***



Outline

- Thermal conductivity of ferroelectrics
  - Single crystals
  - Prior research on ‘extrinsic’ effects
- Our thermal conductivity/ferroelectrics research
  - Grain size scaling effects in $BaTiO_3$
  - Domain boundaries
  - Composition Effects

Composition Effects on PZT Thermal Conductivity

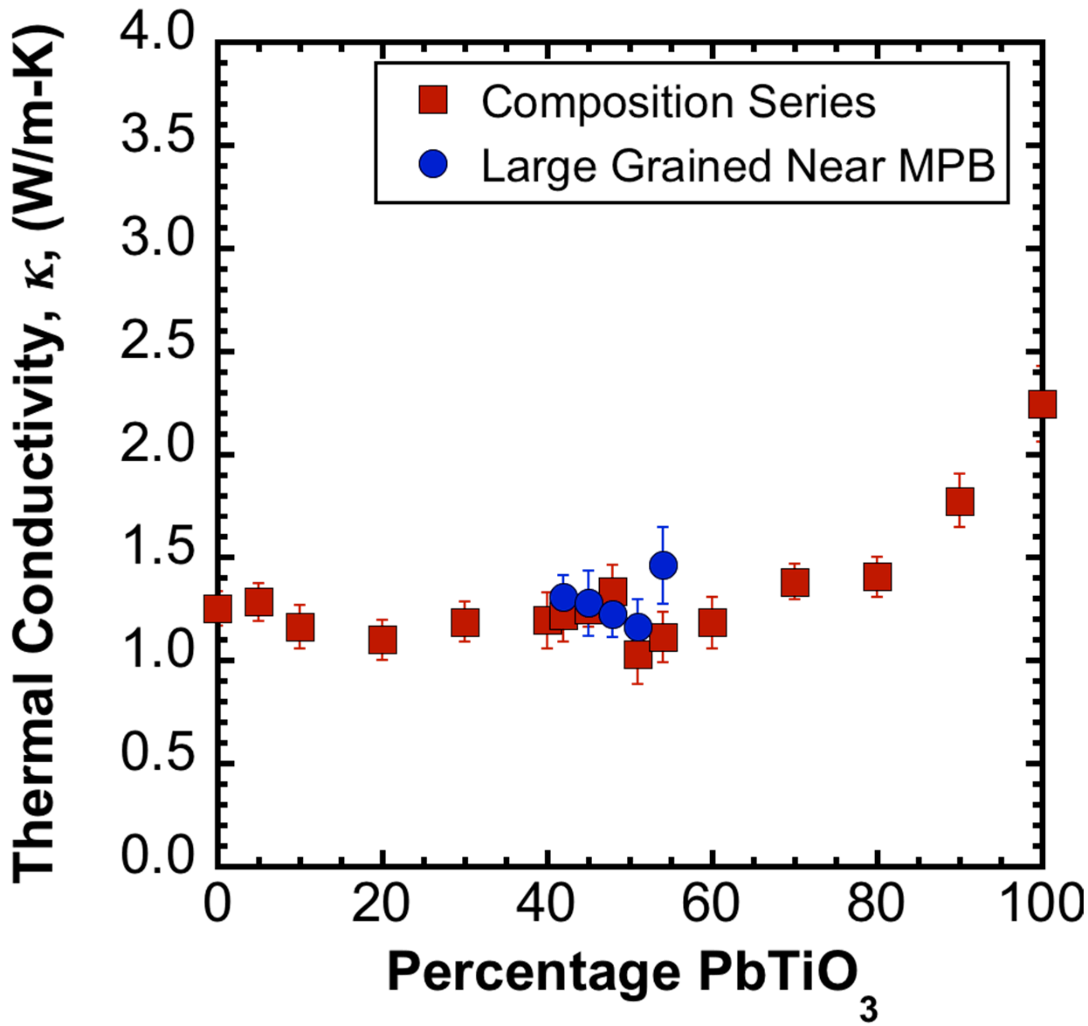
- To increase magnitude of change, must decrease non-boundary scattering:

$$\kappa = \frac{1}{3}\sum_j C_{v,j} v_j^2 \tau_j$$

  - ~~Heat Capacity~~
  - ~~Phonon Velocity~~
  - ***Scattering Times***

$$\tau_j = \tau_{p-p}^{-1} + \tau_a^{-1} + \tau_b^{-1}$$

  - ~~Umklapp~~
  - ~~Boundaries~~
  - ***Alloy -- Composition***



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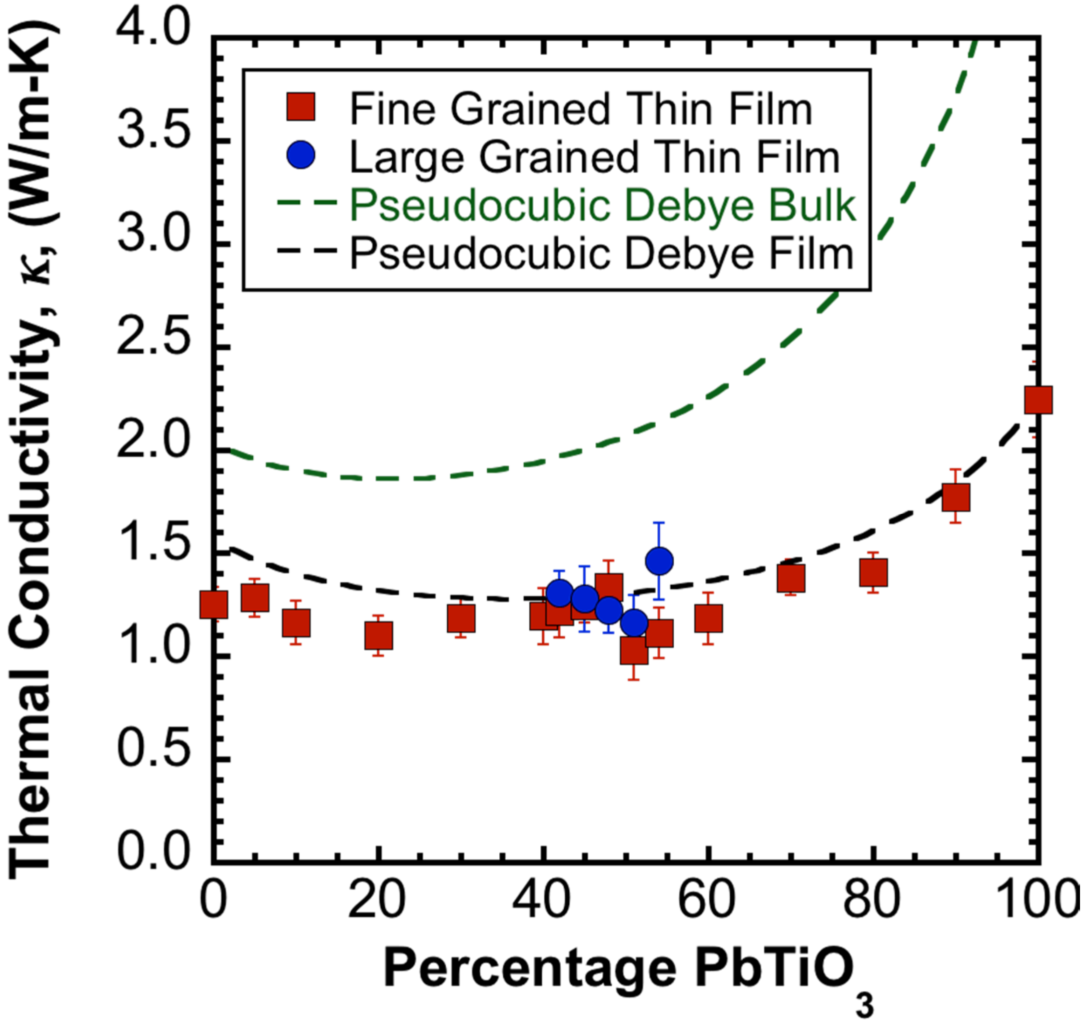
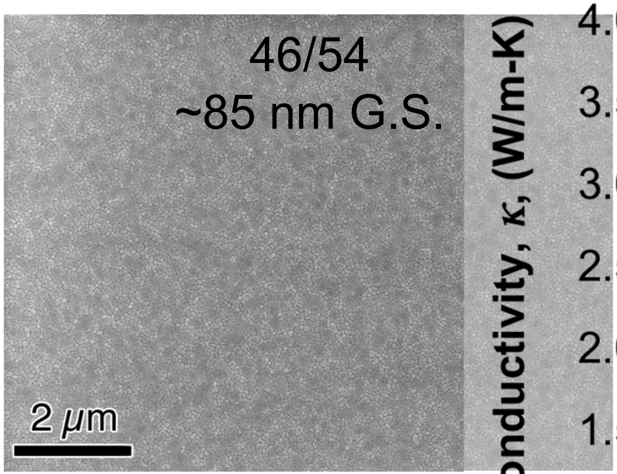
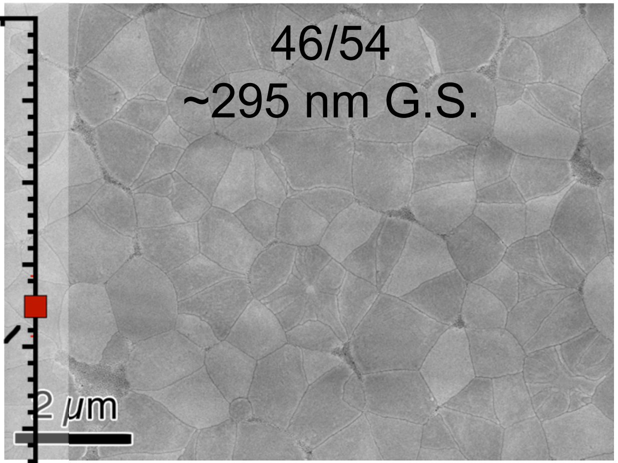
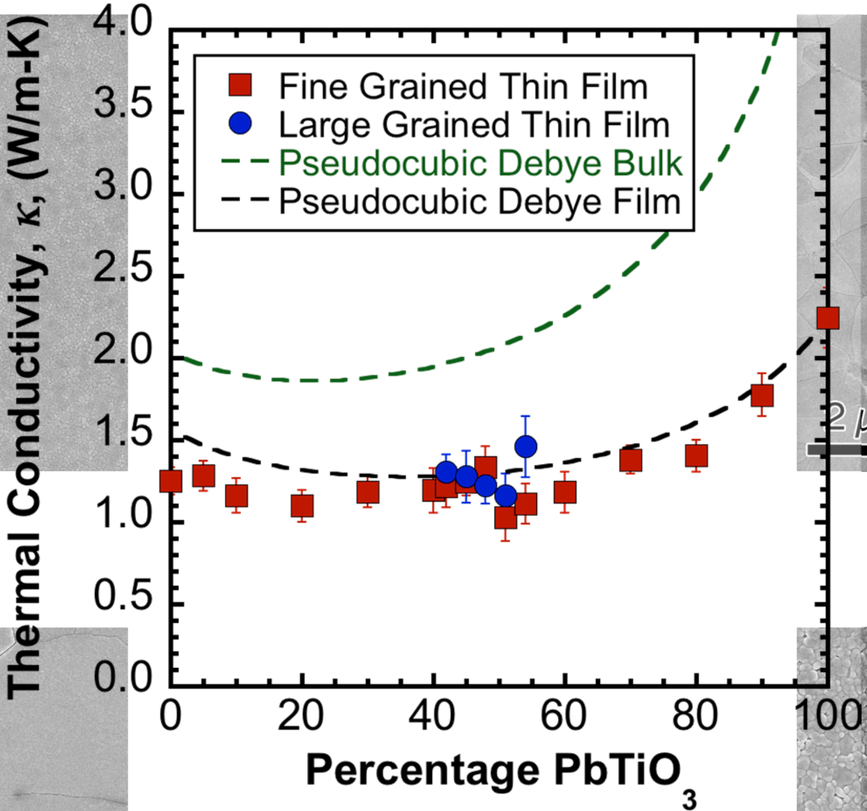
  - ~~Boundaries~~
  - ***Alloy -- Composition***

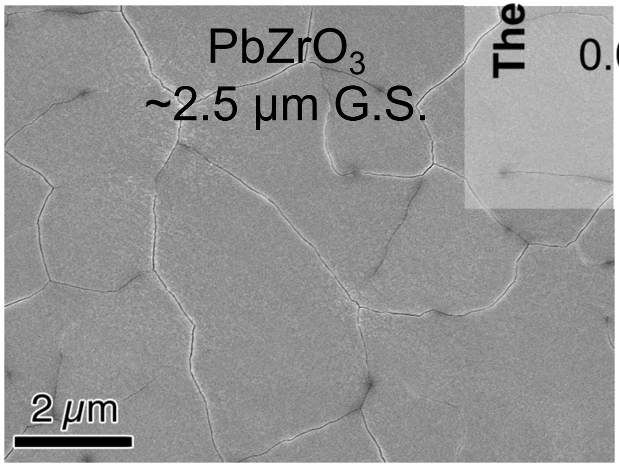


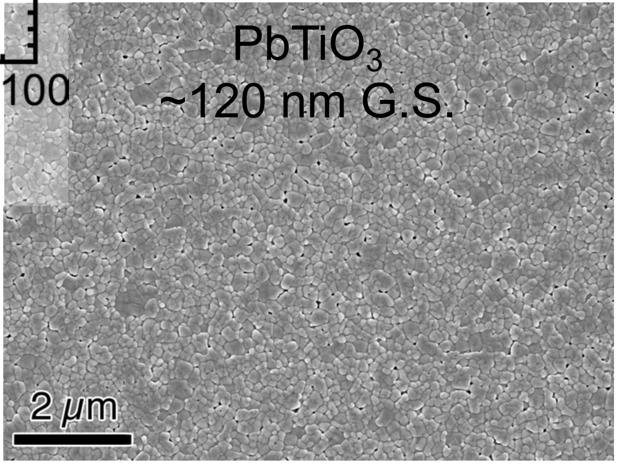
Composition Effects on PZT Thermal Conductivity







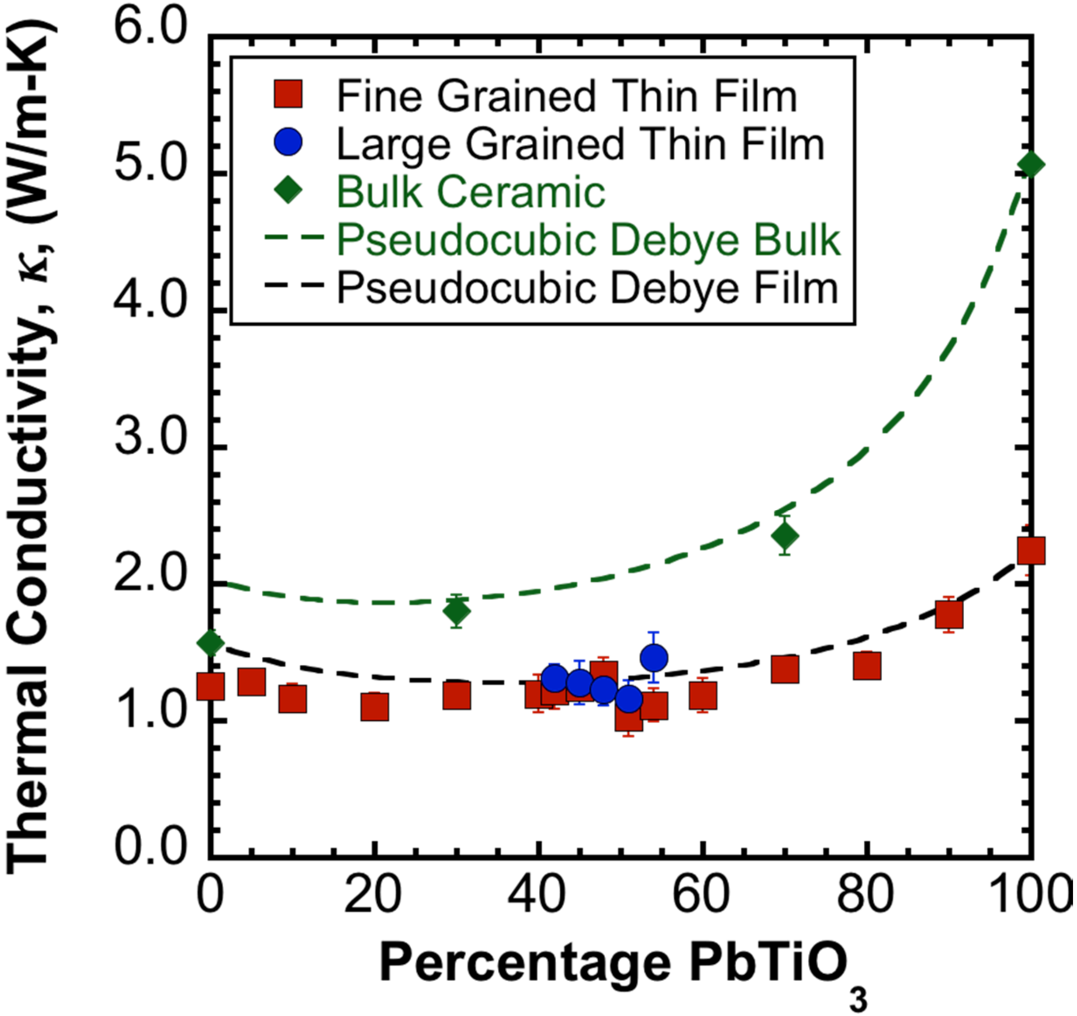




Grain size cannot account for the differences observed

Composition Effects on PZT Thermal Conductivity

- Alloy scattering 'bathtub' effect is present for most compositions
- $PbZrO_3$-rich compositions do not follow expected trend
- Low thermal conductivity also observed for $PbZrO_3$



Composition Effects on PZT Thermal Conductivity

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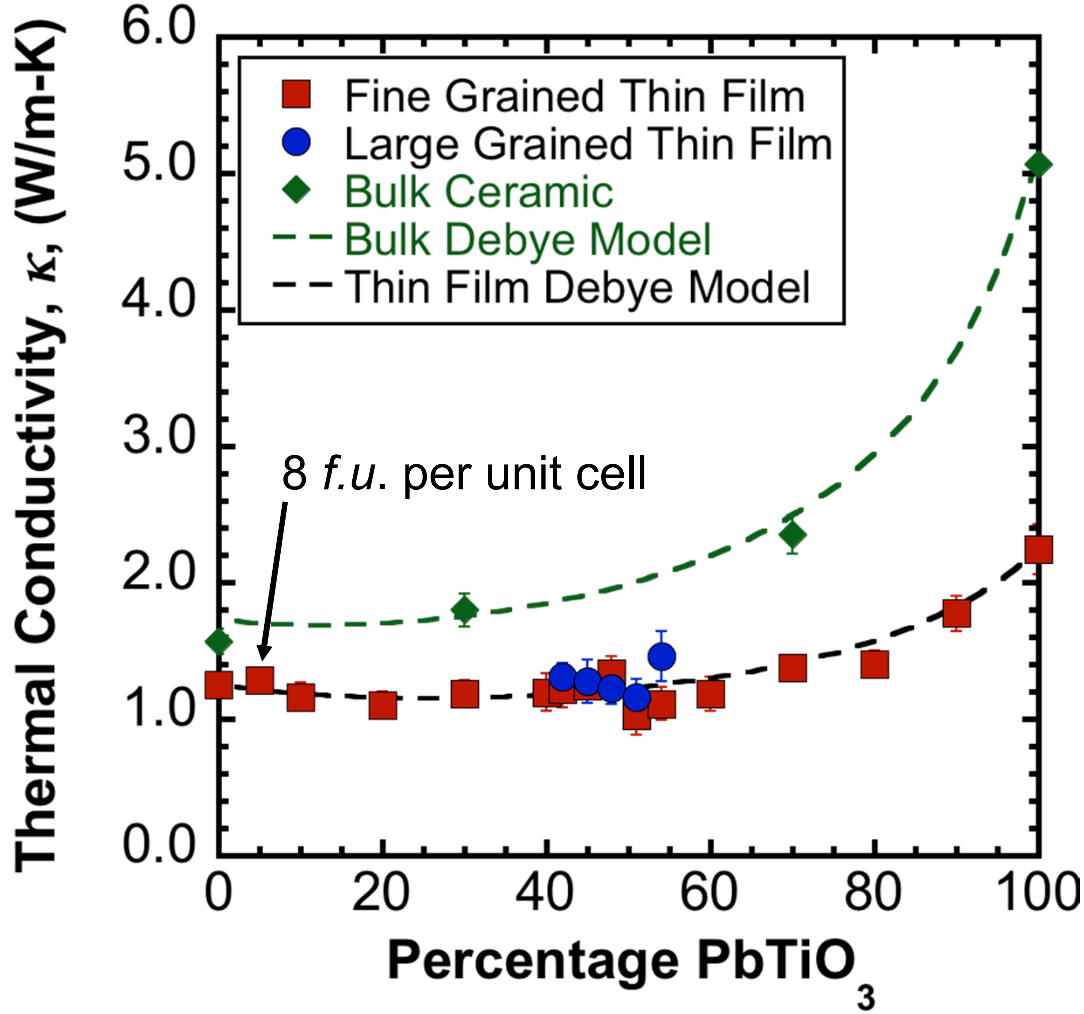
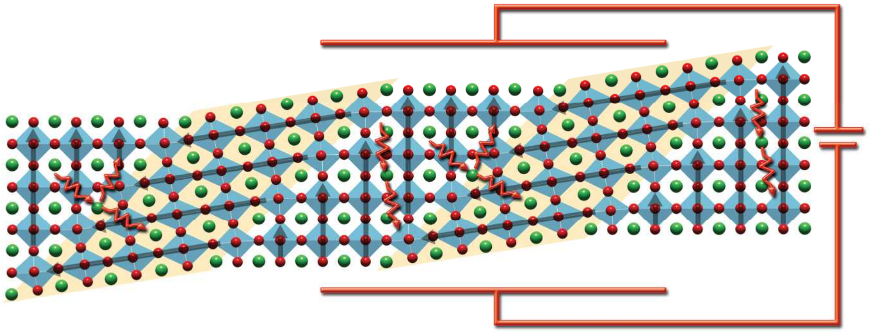
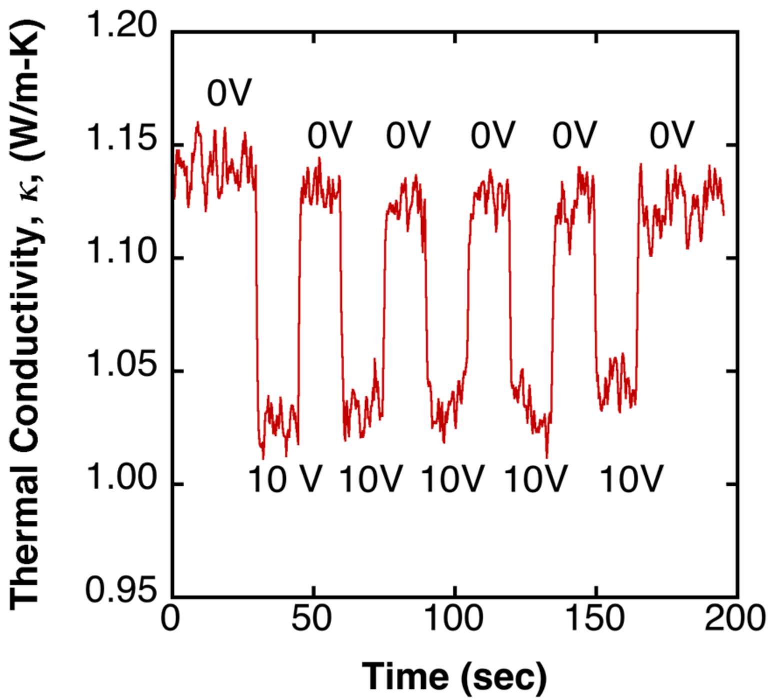
- Alloy scattering 'bathtub' effect is present for most compositions
- $PbZrO_3$-rich compositions do not follow expected trend
- Low thermal conductivity also observed for $PbZrO_3$
- ***Difference is an increased unit cell size and modified Brillouin zone for $PbZrO_3$***



Summary

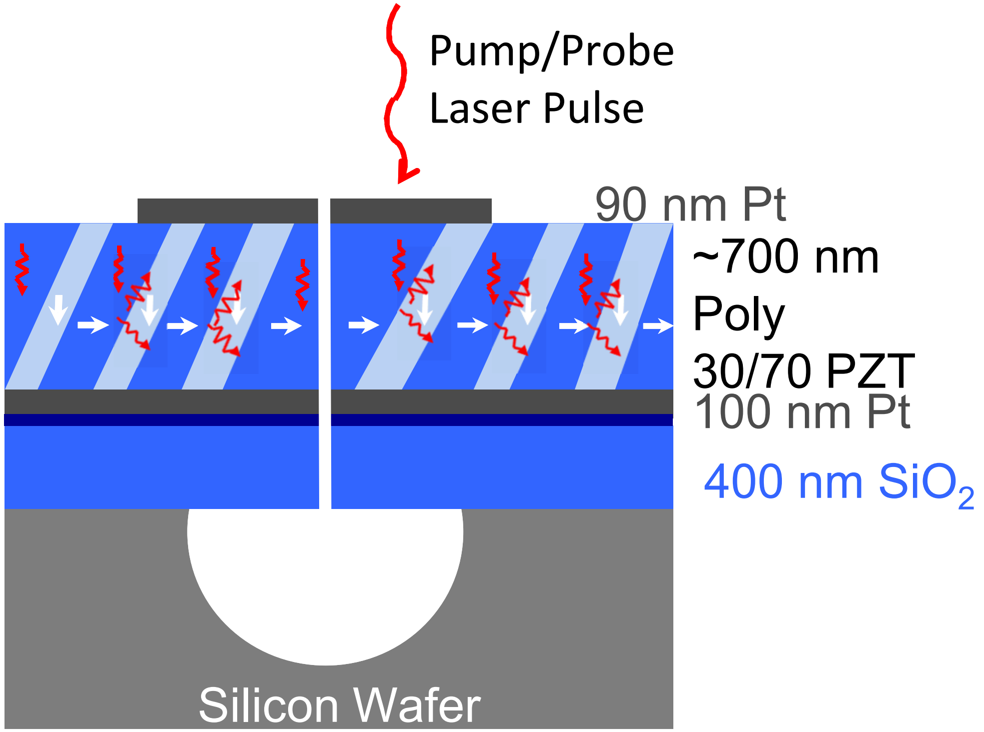
- Grain boundaries, domain boundaries and composition affect heat transfer
- Phonons in ferroelectrics should be considered as a spectrum of wavelengths at a given temperature
- Domain boundaries can scatter phonons *even at room temperature*
- $PbZrO_3$-rich PZT compositions possess very low thermal conductivities owing to unit cell doubling





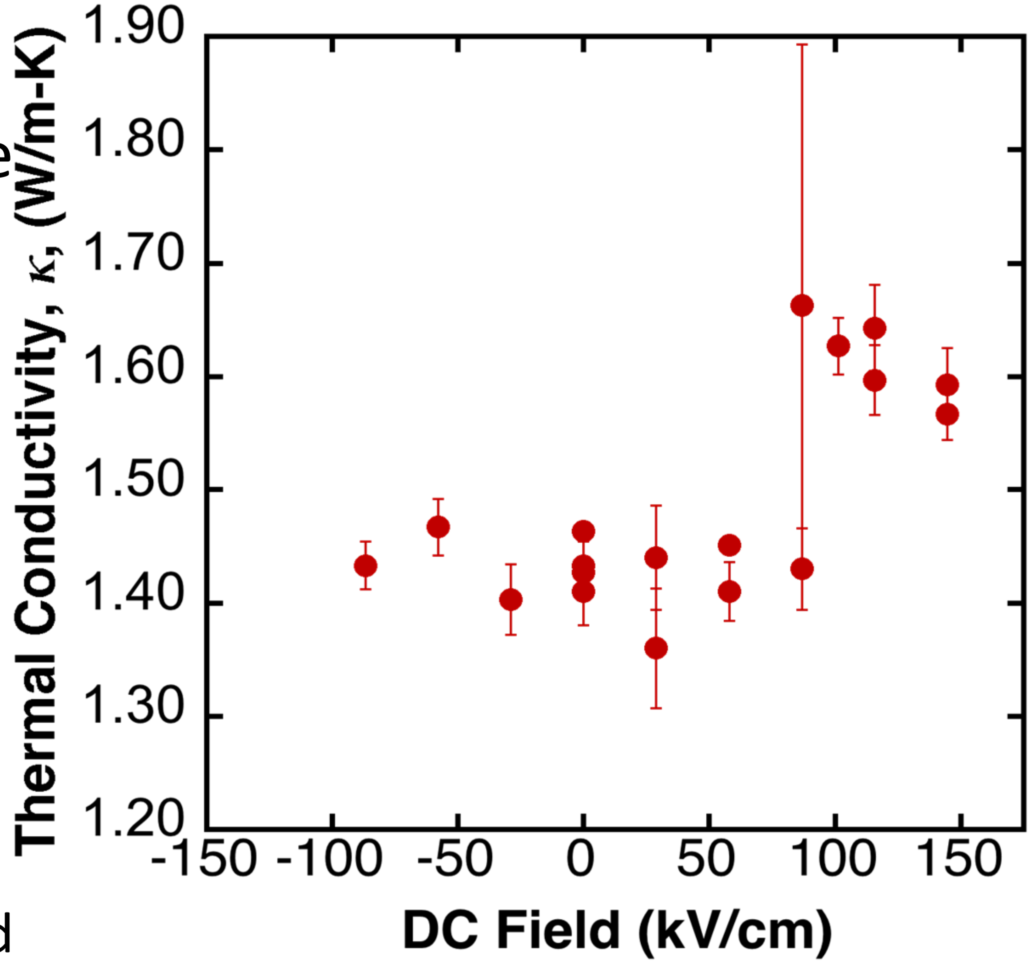
Can We Make Thermal Conductivity Increase?

- Substrate clamping minimizes ferroelastic domain wall motion
- Prevents growth of domains and decrease of domain wall density
- Relieving clamping is expected to increase ferroelastic domain wall mobility
- Released films prepared by XeF_2 etching into a membrane structure



Can We Make Thermal Conductivity Increase?

- Measured thermal conductivity on membrane structure while applying fields
- Observe discontinuous 13% ***increase*** in κ at ~90 kV/cm
- Relieving strain results in increased thermal conduction
  - Most likely due to decreased domain wall density



Can We Make Thermal Conductivity Increase?

- Thermal conductivity change for membrane structures is fast
  - Sub-300 ms timescale
- Response is repeatable
  - Indicates that domain wall densities decrease while under field and increase when field is removed